Synthesis and Characterization of Bi$_2$Te$_3$ Thermoelectric Material Using the Cold Pressing and Sintering Method

Tony Kristiantoro$^{1,2}$, Dedi$^2$, Vivi Fauzia$^1$

1 Departemen Fisika, Fakultas MIPA, Universitas Indonesia, Kampus Baru UI Depok 16424, Indonesia
2 Research Centre for Electronics and Telecommunications – LIPI, Bandung 40135 Indonesia

vivi@sci.ui.ac.id

Abstract. Research on thermoelectric material that could convert heat into electricity is expanding rapidly in the effort to improve efficiency. Bismuth telluride (Bi$_2$Te$_3$ or BT) is one of the most promising thermoelectric materials in converting waste heat into electrical energy; however, oxidation that occurs in the sintering process often decreases efficiency. In this study, we propose the use of activated carbon in the sintering of Bi$_2$Te$_3$, which is prepared using cold pressing to reduce the oxidation effect. Our results show Bi$_2$Te$_3$ possessing a polycrystalline single-phase rhombohedral form with lattice parameters of $a = 4.3841$ Å and $c = 30.4816$ Å. Covering the BT samples with activated carbon during the sintering process improved the power factor of Bi$_2$Te$_3$ from $0.775 \times 10^{-3}$W.m$^{-1}$K$^{-2}$ to $1.0125 \times 10^{-3}$W.m$^{-1}$K$^{-2}$. The improved thermoelectric properties exhibited in the carbon-covered BT samples may be attributed to the absence of an oxidation process occurring during sintering, as indicated by the energy dispersive spectrometry (EDS).

Keywords: Thermoelectric, Bi$_2$Te$_3$, Power factor, Seebeck coefficient

1. Introduction
Thermoelectric material becomes increasingly important in its use as an alternative source of harvesting energy and for energy conversion. The efficiency of thermoelectric materials is determined by the dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, where $S$, $\sigma$, $\kappa$, and $T$ represent the Seebeck coefficient, electrical conductivity, thermal conductivity, and temperature, respectively [1]. Bi$_2$Te$_3$ (BT) has optimal thermoelectric properties and is the best material for thermoelectric cooling and thermoelectric power generation near room temperature [2]. The crystal structure of BT is hexagonal or rhombohedral with the space group of R-3m [3].

The thermoelectric properties of BT-based alloys are influenced by the synthesis method. Besides the use of directed conventional growth from the melt, BT alloys are typically prepared with powder processing that is followed by spark plasma sintering (SPS), hot pressing, or hot extrusion. These methods are expensive and face scale-up challenges [4–10]. In this experiment, we propose the use of cost-effective cold pressing and sintering. However, oxidation occurring in the sintering process often causes a decrease in efficiency. Therefore, we propose the use of activated carbon in the sintering process to reduce the oxidation effect.
2. Experimental method

Commercial BT powder was determined to weigh about 0.5 g before samples were loaded into a steel mold and compacted into rod shapes (5 mm × 12 mm), as shown in Figure 1. Then, one sample was covered with activated carbon in an alumina boat, sintered at 470 °C for 3h in the furnace and then naturally cooled to room temperature.

Measurements of the Seebeck coefficient (S) and electrical resistivity (ρ) were determined using a commercial measurement system (Linseis LSR-4, Germany). The microstructures of samples were observed by X-ray diffraction (XRD D8 Advance, Bruker, Germany) at room temperature using CuKα radiation (λ = 1.5406 Å). The morphology and composition of the samples were observed using field-emission scanning electron microscopy (FESEM) and electron dispersive spectrometry (EDS) (JEOL JSM-IT300, Japan).

![Figure 1. The Bi₂Te₃ bulk sample after the sintering process.](image)

3. Results and discussion

XRD patterns of carbon-covered BT (C-BT), non-covered BT (NC-BT), and commercial BT samples are shown in Figure 2. Using a database Bi₂Te₃ pattern (ICSD#98-004-8203), we determined that all peaks exhibited in samples matched with the peaks of standard patterns, and no peaks were of the secondary phase. The diffraction peaks were indexed to reflect the rhombohedral phase of Bi₂Te₃ with the lattice constants of \(a = 4.3841 \, \text{Å}\) and \(c = 30.4816 \, \text{Å}\).

![Figure 2. XRD patterns of non-covered BT (NC-BT), carbon-covered BT (C-BT), and commercial BT powder.](image)

The morphologies of NC-BT, C-BT, and commercial BT powders are presented in Figure 3 (a,c,e). The material compositions of all samples were then confirmed by the EDS, as shown in
From Figure 3b, it is clear that the NC-BT sample contains oxygen, indicating the occurrence of oxidation during the sintering process.

**Figure 3.** FESEM images and energy dispersive spectrometry (EDS) of non-covered BT (NC-BT) (a, b), carbon-covered BT (C-BT) (c, d), and commercial BT powder (e, f).

Figure 4 shows the temperature-dependent thermoelectric properties of samples that contain the Seebeck coefficient, $S$ (a); the power factor, $S^2\sigma$ (b), and electrical resistivity, $\rho$ (c). The negative
value of the Seebeck coefficient shows that both samples are n-type semiconductors, and the Seebeck coefficient of C-BT is higher than that of the NC-BT samples. Figure 4 also shows that the Seebeck coefficient of each sample increases, from -117.7 to -147 µV/K, as the temperature increases from room temperature to 200 °C. Meanwhile, the $\rho$ values of both samples also increase from 13.81 to 26.72 $\mu\Omega$.m as the temperature increases from 30 °C to 200 °C. This is a typical characteristic of semiconductor materials. The electrical resistivity, $\rho$, of C-BT is lower than that of the NC-BT samples. The higher $S$ and lower $\rho$ values of the C-BT sample results in the power factor, $S^2\sigma$, of the C-BT sample being higher than that of the NC-BT sample, as shown in Figure 4(c). The C-BT sample exhibiting better thermoelectric properties may be attributed to the absence of an oxidation process during sintering, as indicated by the EDS.
Figure 4. Temperature-dependent thermoelectric properties, including (a) Seebeck coefficient $S$; (b) power factor $S^2\sigma$; and (c) electrical resistivity $\rho$ of NC-BT and C-BT samples.

To compare our results with previously published results, a summary of the thermoelectric properties of Bi$_2$Te$_3$ at room temperature is shown in Table 1. Based on this table, it is evident that the power factor of the C-BT sample is higher than that of Bi$_2$Te$_3$ samples prepared using microwave sintering, but it is still lower than that of Bi$_2$Te$_3$ prepared by the spark plasma sintering method. This may be due to the microstructure properties or because the conductivity of our samples is not yet optimal. These results show that covering Bi$_2$Te$_3$ samples with activated carbon during the sintering process is an alternative, low-cost method of improving the thermoelectric properties of Bi$_2$Te$_3$.

| Preparation Method          | Seebeck Coefficient ($\mu$V/K) | Electrical Resistivity ($\mu$Ω.m) | Power Factor ($10^{-3}$W.m$^{-1}$K$^{-2}$) | References        |
|-----------------------------|--------------------------------|----------------------------------|---------------------------------------------|-------------------|
| Spark Plasma Sintering      | 192.15                         | 9.85                             | 2.125                                       | [11]              |
| Microwave Sintering         | 40.3                           | 25.26                            | 0.410                                       | [12]              |
| Carbon Covered              | 117.7                          | 13.81                            | 1.0125                                      | Our work          |

4. Conclusion
We propose the simple and low-cost alternative method for sintering bulk BT samples of covering the BT samples with activated carbon during the sintering process, which our study shows can improve the power factor of Bi$_2$Te$_3$ from $0.775 \times 10^{-3}$W.m$^{-1}$K$^{-2}$ to $1.0125 \times 10^{-3}$W.m$^{-1}$K$^{-2}$. The improved thermoelectric properties of carbon-covered BT samples may be due to the absence of an oxidation process during sintering, as indicated by the EDS.
Acknowledgments
Technical support was provided by the Core Facilities for Thermoelectric Laboratory, Research Centre for Electronics and Telecommunication, Indonesian Institute of Sciences. This research was financially supported by Thematic Research Funding from the Indonesian Institute of Sciences and Grant PITTA 2019 No. 2329/UN2.R3.1/HKP.05.00/2019 from Universitas Indonesia.

References
[1] Dedi, P.C. Lee, C.H. Chien, G.P. Dong, W.C. Huang, C.L. Chen, C.M. Tseng, S.R. Harutyunyan, C.H. Lee, Y.Y. Chen, “Thermoelectric power of single crystalline lead telluride nanowire,” Applied Physic Letter, no.1-5, vol. 103, 2013
[2] DM. Rowe,”CRC Handbook of Thermoelectrics,” 1st ed., New York: CRC Press, 1995 p. 239.
[3] S. Nakajima, “The crystal structure of Bi$_2$Te$_{3-x}$Se$_x$,” Journal Physic and Chemical Solids, vol. 24, pp. 479-485, March 1963
[4] K. Kishimoto and T. Koyanagi, “Preparation of Sintered Degenerate N-Type PbTe with a Small Grain Size and its Thermoelectric Properties,” Journal Applied Physic, vol.92, pp. 2544–2549, 2002
[5] Y. Gelbstein, Z. Dashevsky, and M.P. Dariel, “High performance n-type PbTe-based materials for thermoelectric applications,” Physica B, no. 1-4, vol. 363, pp. 196–205, 2005
[6] J. Yang, R. Chen, X. Fan, W. Zhu, S. Bao, and X. Duan,” Microstructure control and thermoelectric properties improvement to n-type bismuth telluride based materials by hot extrusion,” Journal Alloys and Compounds, vol. 429, pp. 156–162, 2007
[7] P. Zhu, Y. Imai, Y. Isoda, Y. Shinohara, X. Jia, and G. Zou, “Composition-dependent thermoelectric properties of PbTe doped with Bi2Te3,” Journal Alloys and Compounds, vol. 420, pp. 233–236, 2006
[8] Y. Dong, M. McGuire, A. Mailk, and F.J. DiSalvo, “Transport properties of undoped and Br-doped PbTe sintered at high-temperature and pressure ≥4.0 GPa,” Journal of Solid State Chemistry, vol. 182, pp. 2602–2607, 2009
[9] J. Gellman et al., “Thin film thermoelectric devices with high room-temperature figures of merit,” Nature, vol. 55, no. 1, pp. 1–8, 2001
[10] D. Vasilevskiy, R.A. Masut, and S. Turenne, “Thermoelectric and Mechanical Properties of Novel Hot-Extruded PbTe n-Type Material,” Journal of Electronic Materials, Vol. 41, No. 6, 2012
[11] D. Li, R.R. Sun, X.Y. Qin, “Improving thermoelectric properties of p-type Bi2Te3-based alloys by spark plasma sintering,” Progress in Natural Science: Materials International 21, pp. 336–340, 2011
[12] J. A. Zavala, D. Vasilevskiy, S. Turenne, and R.A. Masut, “Microwave Sintering of Bi2Te3- and PbTe-Based Alloys: Structure and Thermoelectric Properties,” Journal of Electronic Materials, Vol. 42, No. 7, pp. 1992-1998, 2013.