

POWER FACTOR OF Bi_2Te_3 AND Sb_2Te_3 ENHANCED BY HIGH DENSITY AND HARDNESS

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Abstract

The power factor is an indicator of the performance of thermoelectric materials. Many researchers improved the thermoelectric conversion efficiency of materials by various techniques such as doping, substitution, and decreasing particle size for dense samples. We present Bi_2Te_3 and Sb_2Te_3 materials prepared by hot pressing method at 673 K for 2 h in Ar atmosphere. Bulk samples were investigated for their crystalline structure, hardness, and power factor by XRD, micro-Vickers hardness, and ZEM-3, respectively. The Seebeck coefficient, electrical resistivity, and power factor of n- Bi_2Te_3 and p- Bi_2Te_3 bulk samples were higher than literature data in the same temperature range of 325 to 475 K. The higher power factor value of Bi_2Te_3 and Sb_2Te_3 bulk samples of this study have resulted from the high density and high micro-Vickers hardness of the samples.

Keywords: Bi_2Te_3 and Sb_2Te_3 ; micro-Vickers hardness; power factor; thermoelectric materials

Introduction

Thermoelectric (TE) materials have been the topic of intensive research due to their unique capability of directly converting heat into electricity power into cooling or heating. These materials can reduce carbon emissions by converting waste heat TE materials for commercial application of low

temperature TE cooling and generators (Yim and Rosi, 1972). The performance TE materials are related to a parameter called the dimensionless figure of merit: dimensionless figure of merit as following:

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$$zT = \frac{S^2 T}{\rho K}$$

where, S is Seebeck coefficient, ρ is electrical resistivity, κ is thermal conductivity, and T is absolute temperature (Snyder and Toberer, 2008; Li *et al.*, 2010; Par'as-Hernandez *et al.*, 2020). The PF is directly proportional to zT and describes the electronic transport of a materials which is useful to select the class of potential TE materials. The PF can be enhanced based on various strategies such as band engineering and exploitation of complex band structure. The TE power generation efficiency is given by the band structure (Cao *et al.*, 2017; Zhou *et al.*, 2018). Therefore, to improve efficiency, the factors such as large PF and substantial differences between and must be taken into account. To order to increase PF , low must be maintained while minimized S and ρ . Bi_2Te_3 based materials are the best TE materials operating at a low temperature and they were widely used for many TE applications. The crystal structure of these materials is a hexagonal or rhombohedral structure, space group number 166 and lattice parameter $a = 0.438$ and $c = 30.48$ nm (Feutelais *et al.*, 1993). Bi_2Te_3 and Sb_2Te_3 was studied with various method such as solid state rection (SSR) (Hailiang *et al.*, 2020), spark plasma (SPS) (Dong *et al.*, 2010) and hot pressing (HP) (Yang *et al.*, 2000). TE properties of Bi_2Te_3 based alloys are intensely affected by the preparation process which are most widely used TE materials at near room temperature. Li *et al.* (2011) report TE properties of Bi_2Te_3 and Sb_2Te_3 prepared by HP and characterization TE properties (Li *et al.*, 2011). The ρ was significantly increased and thermal conductivity was decreased, with a maximum $zT = 1.33$ at 398 K (Kalantar-Zade *et al.*, 2006). Xie *et al.* (2010) proposed newly modified solvothermal/SPS process to synthesize Bi-Sb-Te hexagonal nanoplatelets. The low zT achieved 0.51

at 375 K was attributed to a low PF although great low hardness and density (Xie *et al.*, 2010). Mukherjee *et al.* (2018) have reported on the enhancement of the TE properties of Sb_2Te_3 by micro-Vickers hardness (Mukherjee *et al.*, 2018). However, investigation and optimization of PF in Bi_2Te_3 and Sb_2Te_3 materials is very important from the point of view of application.

In the present work, we attempted to prepare Bi₂Te₃ and Sb₂Te₃ bulk samples using HP sintering process. The *S* of bulk sample were systematically investigated from the viewpoint of high density and hardness to increased *PF* in Bi₂Te₃ and Sb₂Te₃ bulk sample.

Materials and Methods

The basics of experimental procedures were described in our previous study (Yang *et al.*, 2006). In brief, Bismuth (Bi), Antimony (Sb) and Tellurium (Te) powder, 99,999% in purity were prepared to have composition of Bi_2Te_3 and Sb_2Te_3 . The powder of Bi, Sb and Te were mixed in planetary ball mill at 350 rpm for 10 h under Ar atmosphere then mixed elements were load into quartz tube and heated to 1,073 K for 10 h in Ar atmosphere. The melted ingots were crushed by ball milling for 2 h under Ar atmosphere (Lee *et al.*, 2021). The powder of Bi_2Te_3 and Sb_2Te_3 were pressed into pellet in cylindrical graphite die 4 cm at 673 K under 60 MPa for 2 h step up 5°C min^{-1} in vacuum (Fan *et al.*, 2015; Kim *et al.*, 2017). The density of sample was measured by Archimedes principle. The micro hardness of bulk specimens was carried out on a micro-Vickers hardness tester (Shimadzu) at room temperature. Bulk sample was analyzed by using an X-ray diffractometer (XRD-6100 Shimadzu, Japan) at room temperature using $\text{CuK}\alpha_1$ radiation (1.54186 Å) to determine the crystal structures. The sintered specimens were cut into rectangular pieces ($3\times3\times15\text{ mm}^2$) used to measure the S and ρ using a four-probe method (ULVAC-RIKO, ZEM-3) from 325 to 475 K.

Results and Discussion

The XRD patterns of Bi₂Te₃ and Sb₂Te₃ showed relationship of diffraction angle and intensity of these materials as shown in Figure 1(a-b). The XRD patterns showed the single Bi₂Te₃ phase with a rhombohedral structure space group in $R\bar{3}m$ corresponds with the standard patterns of Bi₂Te₃ (JCPDS#15-0863) and rhombohedral structure: a = b = 0.431 nm and c = 3.044 nm (Dong *et al.*, 2010). The XRD patterns of Sb₂Te₃ bulk sample

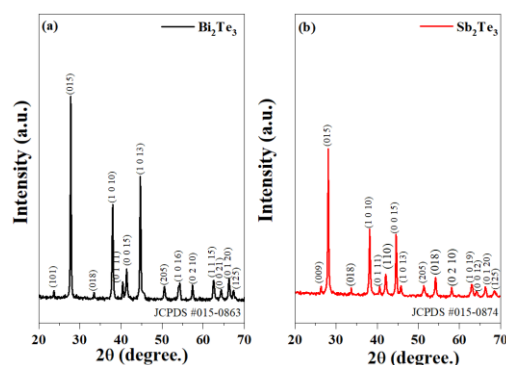


Figure 1. (a) The XRD patterns of Bi₂Te₃ and (b) Sb₂Te₃ bulk samples

show all the diffraction peaks can be indexed according to the crystallographic structure of Sb_2Te_3 (JCPDS #015-0874). The (015), (1 0 10) and (0 0 15) peaks are the dominant peaks, which indicate a preferential growth of the grains along these directions. The peak at around 28° from the Te element confirms that the sample is Te-rich as shown in Figure 1(b).

The temperature dependence of the S , ρ , and PF for HP sintered samples of Bi_2Te_3 investigated are presented in Figure 2(a). The negative value indicated that sample were n -type semiconductors. It can be assumed that a higher density and a higher hardness are obtained, which exhibited a high S with a low ρ , which is shown in Table 1. The density effects of all sample could be excluded because the relative density was close to each other and obtained more than 99%. The S of the sintered sample was observed to decrease with increasing temperature from $-249 \mu\text{V K}^{-1}$ at 325 K to $-183 \mu\text{V K}^{-1}$ at 475 K corresponding with (Lee *et al.*, 2014; Liu *et al.*, 2017). The ρ of Bi_2Te_3 sample increased with increasing temperature, to reach a maximum value and then was observed to decreased with further increase in temperature. The ρ value show $0.9 \times 10^{-5} \Omega \text{ m}$ at 325 K to $1.1 \times 10^{-5} \Omega \text{ m}$ at 475 K as shown in Figure 2(b). The temperature dependence of the PF on the Bi_2Te_3 were investigated sample. The PF value decreased with increasing temperature from $6.2 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-2}$ at 325 K to $2.9 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-2}$, due to result mainly from high density and hardness affect high S , low ρ and high PF respectively as shown in Figure 2(c).

Table 1. Lattice parameter, bulk density, relative density and micro-Vickers hardness of Bi_2Te_3 and Sb_2Te_3 bulk samples

Sample	Lattice parameter (nm)		Bulk density (g/cm^3)	Relative density (%)	Vickers hardness (GPa)	Ref.
	a = b	c				
Bi_2Te_3	0.431	3.044	7.42	99.8	68	(Hu <i>et al.</i> , 2018)
Sb_2Te_3	0.448	3.087	7.32	99.9	70	(Madavali <i>et al.</i> , 2021)

The temperature dependence on the S of the Sb_2Te_3 bulk sample at the temperature range 325 to 475 K compared with literature data as shown in Figure 3(a). The S value of Sb_2Te_3 shown positive value indicate that p -type and increased with increasing temperature, reaching a maximum value before decreasing with rising temperature. This kind of behaviour was observed in previous report (Hamawandi *et al.*, 2020). The increased S values

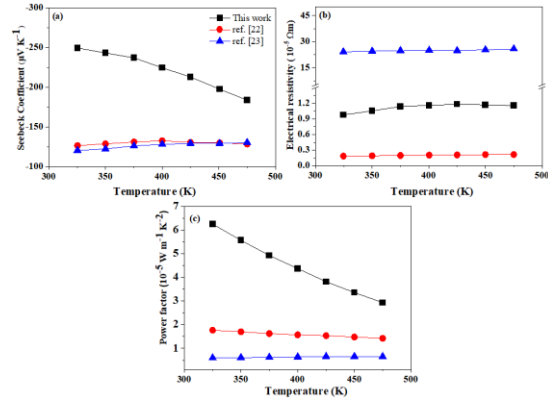


Figure 2. (a) The temperature dependent on Seebeck coefficient, (b) electrical resistivity, and (c) power factor of Bi_2Te_3 bulk samples

due to decreasing carrier concentration, and decreased values due to increase carrier concentration (Kumar *et al.*, 2019). The S value of Sb_2Te_3 sample from $197 \mu\text{V K}^{-1}$ at 325 K to $186 \mu\text{V K}^{-1}$ at 475 K. However, these values are less than those of sample, although the Sb_2Te_3 bulk sample had S value that were comparable to those in (Dharmaiah *et al.*, 2016). The ρ of Sb_2Te_3 sample increased with increasing temperature, which indicates that the bulk materials exhibit a temperature dependence of the ρ that is described by metallic-like or degenerate semiconductor behaviour from $0.6 \times 10^{-5} \Omega \text{ m}$ at 325 K to $1.2 \times 10^{-5} \Omega \text{ m}$ at 475 K, as shown in Figure 3(b). Moreover, the evaluated PF value of Sb_2Te_3 sample decreased with increasing temperature from $33.3 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-2}$ at 325 K to $20.6 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-2}$ at 475 K, as shown in Figure 3(c).

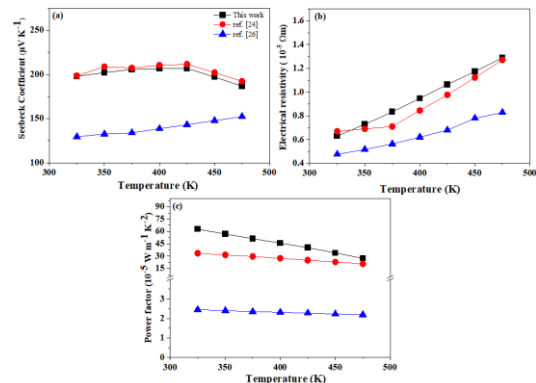


Figure 3. (a) The temperature dependent on Seebeck coefficient, (b) electrical resistivity, and (c) power factor of Sb_2Te_3 bulk samples

Conclusions

In this study, we investigated the effects of density and hardness on the power factor of Bi₂Te₃ and Sb₂Te₃ sintered samples. A significantly higher *S* was obtained in samples due to the high relative density and hardness more than 99%. The maximum *S* value reached -249 $\mu\text{V K}^{-1}$ at 325 K in Bi₂Te₃, while Sb₂Te₃ bulk samples were around and 197 $\mu\text{V K}^{-1}$ at 325 K, the maximum *PF* value is $6.2 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-2}$ at 325 K of Bi₂Te₃, while Sb₂Te₃ bulk samples were around and $33.3 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-2}$ at 325 K. Which demonstrates that the high density and hardness can enhance *PF* of Bi₂Te₃ and Sb₂Te₃ bulk samples.

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References

- Cao, X.-H., Zhou, W.-X., Chen, C.-Y., Tang, L.-M., Long, M., and Chen, K.-Q. (2017). Excellent thermoelectric properties induced by different contact geometries in phenalenyl-based single-molecule devices. *Scientific Reports*, (7):10842. <https://doi.org/10.1038/s41598-017-11224-x>
- Dharmaiah, P., Kim, H.-S., Lee, C.-H., and Hong, S.-J. (2016). Influence of powder size on thermoelectric properties of p-type 25% Bi₂Te₃-75% Sb₂Te₃ alloys fabricated using gas-atomization and spark-plasma sintering. *Journal of Alloys and Compounds*, 686:1-8. <https://doi.org/10.1016/j.jallcom.2016.05.340>
- Dong, G.H., Zhu, Y.J., and Chen, L.D. (2010). Microwave-assisted rapid synthesis of Sb₂Te₃ nanosheets and thermoelectric properties of bulk samples prepared by spark plasma sintering. *Journal of Materials Chemistry*, 20:1976-1981. <https://doi.org/10.1039/b915107a>
- Fan, X., Yang, F., Rong, Z., Cai, X., and Li, G. (2015). Characterization and thermoelectric properties of Bi_{0.4}Sb_{1.6}Te₃ nanostructures prepared by mechanical alloying and microwave activated hot pressing. *Ceramics International*, 41(5):6817-6823. <https://doi.org/10.1016/j.ceramint.2015.01.130>
- Feutelais, Y., Lendre, B., Rodier, N., and Agafonov, V. (1993). A study of phases in the bismuth-telluride system. *Materials Research Bulletin*, 28(6):591-596. [https://doi.org/10.1016/0025-5408\(93\)90055-I](https://doi.org/10.1016/0025-5408(93)90055-I)
- Hailiang, H.G., Chen, W.R., Gong, Y., Yang, M., Zeng, Y., Huang, Z., Qi, J., and Lu, S.Q. (2020). Tiecheng, Synthesis, Characterization and sintering of Li₂TiO₃ nanoparticles temperature solid-state reaction. *Ceramics International*, 46:1816-1823. <https://doi.org/10.1016/j.ceramint.2019.09.157>
- Hamawandi, B., Ballikaya, S., Batili, H., Roosmark, V., Orlovská, M., Yusuf, A., Johnsson, M., Szukiewicz, R., Kuchowicz, M., and Toprak, M.S. (2020). Facile solution synthesis, processing and characterization of n- and p-type binary and ternary Bi-Sb tellurides. *Applied Sciences*, 10(3):1178. <https://doi.org/10.3390/app10031178>
- Hu, J., Fan, X.A., Jiang, C., Feng, B., Xiang, B.Q., Li, G., He, Z., and Li, Y. (2018). Introduction of porous structure: A feasible and promising method for improving thermoelectric performance of Bi₂Te₃ based bulks. *Journal of Materials Science & Technology*, 34(12):2458-2463. <https://doi.org/10.1016/j.jmst.2018.05.010>
- Kalantar-Zade, K., Wlodarski, W., Li, L., Kandasamy, S., and Rosengarten, G. (2006). A thermoelectric transducers based on bismuth telluride thin films for H₂ gas sensing. *Journal of Rare Metal Materials and Engineering*, 35(1):190-194.
- Kim, Y.M., Lydia, R., Kim, J.-H., Lin, C.-C., Ahn, K., and Rhyee, J.-S. (2017). Enhancement of thermoelectric properties in liquid-phase sintered Te-excess bismuth antimony tellurides prepared by hot-press sintering. *Acta Materialia*, 135:297-303. <https://doi.org/10.1016/j.actamat.2017.06.036>
- Kumar, S., Faraz, M., and Khare, N. (2019). Enhanced thermoelectric properties of Sb₂Te₃-graphene nanocomposite. *Materials Research Express*, 6:085079. <https://doi.org/10.1088/2053-1591/ab1d1f>
- Lee, G.-E., Kim, I.-H., Lim, Y.S., Seo, W.-S., Choi, B.-J., and Hwang, C.-W. (2014). Preparation and Thermoelectric properties of Bi₂Te₃-Bi₂Se₃ solid solutions. *Journal of the Korean Physical Society*, 64:1416-1420. <https://doi.org/10.3938/jkps.64.1416>
- Lee, K.H., Kim, Y., Kim, D.H., Park, C.O. Kim, H.-S., and Kim, S.-I. (2021). Studies on phase formation behavior and thermoelectric transport properties of Cu-doped Bi₂Te₃-Bi₂Se₃ system. *Journal of Materials Research and Technology*, 15:4781-4789. <https://doi.org/10.1016/j.jmrt.2021.10.049>
- Li, D., Sun, R.R., and Qin, X.Y. (2011). Thermoelectric properties of p-type (Bi₂Te₃)_x(Sb₂Te₃)_{1-x} prepared by spark plasma sintering. *Intermetallics*, 19(12):2002-2005. <https://doi.org/10.1016/j.intermet.2011.07.010>
- Li, J.-F., Liu, W.-S., Zhao, L.-D., and Zhou, M. (2010). High-performance nanostructured thermoelectric materials. *NPG Asia Materials*, 2:152-158. <https://doi.org/10.1038/asiamat.2010.138>
- Liu, R., Tan, X., Ren, G., Liu, Y., Zhou, Z., Liu, C., Lin, Y., and Nan, C. (2017). Enhanced thermoelectric performance of Te-Doped Bi₂Se_{3-x}Te_x bulks by self-propagating high-temperature synthesis. *Crystals*, 7(9):257. <https://doi.org/10.3390/cryst7090257>
- Madavali, B., Lee, C.-H., Han, J.-G., Kim, D.H., Kim, J.T., Song, G., Lee, J.K., and Hong, S.-J. (2021). Investigation of homogeneity in microstructure and thermoelectric properties at various positions in high-thickness sintered bulks of p-type 20%Bi₂Te₃-80%Sb₂Te₃ alloys. *Journal of Materials Science: Materials in Electronics*, 32:16302-16310. <https://doi.org/10.1007/s10854-021-06178-w>
- Mukherjee, S., Femi, O.E., Chetty, R., Chattopadhyay, K., Suwas, S., and Mallik, R.C. (2018). Microstructure and Thermoelectric Properties of Cu₂Te-Sb₂Te₃ Pseudo-binary System. *Applied Surface Science*, 449:805-814. <https://doi.org/10.1016/j.apsusc.2017.11.198>
- Parás-Hernández, F.U., Fabián-Mijangos, A., Cardona-Castro, M.A., and Alvarez-Quintana, J. (2020). Enhanced performance nanostructured thermoelectric converter for self- powering health sensors. *Nano Energy*, 74:104854. <https://doi.org/10.1016/j.nanoen.2020.104854>

- Snyder, G.J. and Toberer, E.S. (2008). Complex thermoelectric materials. *Nature Materials*, (7):105-144. <https://doi.org/10.1038/nmat2090>
- Xie, W., He, J., Kang, H.J., Tang, X., Zhu, S., Lever, M., Wang, S., Copley, J.R., Brown, C.M., Zhang, Q., and Tritt, T.M. (2010). Identifying the specific nanostructure responsible for the high thermoelectric performance of $(\text{Bi,Sb})_2\text{Te}_3$ nanocomposites, *Nano Letters*, 10(9):3283-3289. <https://doi.org/10.1021/nl100804a>
- Yang, J., Aizawa, T., Yamamoto, A., and Ohta, T., (2000) Thermoelectric properties of p-type $(\text{Bi}_2\text{Te}_3)_x(\text{Sb}_2\text{Te}_3)_{1-x}$ prepared via bulk mechanical alloying and hot pressing. *Journal of Alloys and Compounds*, 309(1-2):225-228. [https://doi.org/10.1016/S0925-8388\(00\)01063-X](https://doi.org/10.1016/S0925-8388(00)01063-X)
- Yang, J.Y., Fan, X.A., Chen, R.G., Zhu, W., Bao, S.Q., and Duan, X.K., (2006). Consolidation and thermoelectric properties of n-type bismuth telluride based Materials by Mechanical alloying and hot pressing. *Journal of Alloys and Compounds*, 416(1-2):270-273. <https://doi.org/10.1016/j.jallcom.2005.08.054>
- Yim, W.M. and Rosi, F.D. (1972). Compound tellurides and their alloys for peltier cooling: A review. *Solid-State Electronics*, 15(10):1121-1140. [https://doi.org/10.1016/0038-1101\(72\)90172-4](https://doi.org/10.1016/0038-1101(72)90172-4)
- Zhou, J., Zhu, H., Liu, T.H., Song, Q., He, R., Mao, J., Liu, Z., Ren, W., Liao, B., Singh, D.J., Ren, Z., and Chen, G. (2018). Large thermoelectric power factor from crystal symmetry protected non-bonding orbital in half-Heuslers. *Nature Communications*, (9):1-9. <https://doi.org/10.1038/s41467-018-03866-w>