EDUZONE: International Peer Reviewed/Refereed Multidisciplinary Journal (EIPRMJ), ISSN: 2319-5045
Volume 6, Issue 1, January-June, 2017, Impact Factor: 4.295, Available online at: www.eduzonejournal.com

Enhancement of Thermoelectric Figure-of-Merit in P-type BiSbTe Nanocomposite Alloy

Surajit Chakrabarty[1*], Shoumik Bhattacharjee[2], Mitun Lal Dey[3], Arup Purkayastha[4]

[1*]Department of Chemistry, Government Degree College, Dharmanagar, North Tripura-799250, India
[2]Department of Chemistry, Ledrai Dewan Class XII School, Machmara, Unakoti, Tripura-799263, India
[3]Department of Chemistry, Ujan Baghaicherra High School, Pecharthal, Unakoti, Tripura-799263, India
[4]Nanoinfotech, Bangalore, India

ABSTRACT

We have synthesized nanoparticles of P-type bismuth antimony telluride ($Bi_{40-X}Sb_XTe_{60}$), where x = 25-30, by wet chemical method which exhibits significant enhancement in the figure of merit ZT upto 1.51. Thermoelectric materials BiSbTe nanocomposite have better compressive strength compared to conventional bulk BiSbTe and hence we are able to enhance ZT by increasing power factor. The enhancement of ZT is due to very low thermal conductivity. ZT approaches maximum with nano to bulk ratio (90:10) which indicates in reverse nanocomposite small amount of bulk is sufficient to raise the power factor.

Keywords: Figure- of -Merit (ZT), Bismuth Antimony Telluride , Thermoelectric, Nanocomposite.

INTRODUCTION

Thermoelectric materials is considered to have key role in power generation and cooling applications [1-2]. It can have huge impact on environment, since thermoelectric materials don't use any harmful refrigerants for cooling and generate electricity from industrial waste heat [3]. However large scale commercial application of thermoelectric materials hitherto is limited due to their low figure of merit, around 1.0 [4]. Performance of thermoelectric materials is measured by dimensionless number, figure of merit ZT, which is defined as, $ZT = \frac{\alpha^2\sigma}{k}$T, where α - Seebeck coefficient, σ - electrical conductivity and κ - thermal conductivity [5-6]. However, increasing ZT has become challenging because the thermal conductivity κ, Seebeck coefficient α, electrical conductivity σ, follow opposing trends [7]. Bismuth telluride based thermoelectric materials are considered as one of the best room temperature thermoelectric material, commonly used for cooling application. Despite all effort, ZT of bismuth telluride based materials at room temperature remains at 0.9 to 1.0. While, ZT = 4 is required for the replacement of compressor based refrigeration or meaningful power generation application [8-9]. In this work, nanocomposite thermoelectric materials based on BiSbTe are sought to enhance ZT by decreasing thermal conductivity through interfacial phonon scattering, at the same time increasing number of density of states near Fermi level in nanostructure present in the nanocomposite to enhances Seebeck coefficient [10-12]. While presence of bulk will provide better connectivity with nanostructures which will help in retention of superior electrical conductivity [13-14].

In this work we observe better compressive strength which will help to reduce wear and damage in harsh condition. Thus, during cutting of p-legs to make thermoelectric module, nanocomposite materials will produce high yield, compared to conventional bulk materials. By this process, we are able to enhance ZT by 20 - 50% in composite, by increasing power factor($\sigma\alpha^2$) compare to the ZT of parent nano and parent bulk bismuth antimony telluride. This clearly indicates nanocomposite route can enhance ZT. This is unique nanocomposite, where nanomaterial is used as matrix (host) and microparticles as a inclusion (guest). Presence of bulk in the nanomatrix leads to the formation of randomized short range sheet nanostructure in the nanocomposite. ZT approaches maximum with nano to bulk ratio (90:10). Our method is very facile, highly reproducible and cost effective than any reported p-type system [15-21].

Experimental:

Elemental Powders of Bi (99.99%), Sb (99.9%), Te(99.5%), Orthotelluric acid (H_6TeO_6, 98%), Antimony Acetate , Hydrazine hydrate, ethylene glycol were obtained from Sigma Aldrich and used without further purification.

Microanalytical Characterization:
The nanoparticle morphology and structure were characterized using a combination of scanning electron microscopy (SEM), X-ray diffraction and X-ray. SEM were carried out in a Hitachi SN3200 operating 0.3-30 Kv. The as-prepared

nanoparticles were dispersed in hexane, sonicated for few seconds, and were drop cast eith on a Si(001) wafer piece for SEM. The powder XRD of bismuth antimony telluride was carried out in Rigaku X-ray diffractograms and were collected using a smart web X-ray diffractmeter with Cu K_α (λ= 0.154 nm) radiation.

Synthesis of BiSbTe nanoparticles A:

We have synthesized nanoparticles of bismuth antimony telluride ($Bi_{40-X}Sb_XTe_{60}$), where x = 25-30, by wet chemical method which is amenable for large scale synthesis of tellurium and antimony along with bismuth powder reacted in ethylene glycol. The reaction temperatures were in the range of 110-180 ^oC. Hydrazine hydrate was used as reducing agent. The obtained nanoparticles were purified by repeated centrifuging and washing with water and finally dried under vacuum.

Synthesis of Bulk bismuth antimony telluride:

Bulk bismuth antimony tellurides were prepared from constituent metals, viz., bismuth, antimony and tellurium by melting route. Finally, zone melting was carried out to obtain single crystals bismuth antimony telluride. The single crystal material was crushed to obtain bulk powder.

Hot pressing nano powder A:

The dried nanoparticles were placed in graphite die and pressed under vacuum to obtain compact pellet (B). The hot pressing was carried out at a temperature (300-500 ℃) and force (150- 375 Kg/cm^2) for the duration of 2 h to 4 h.

Preparation of nanocomposite A:

As prepared nanoparticles and bulk bismuth antimony telluride powders were mixed in different weight percentage ratio (50:50, 60: 40, 70: 30, 80: 20, 90:10). Pestle and mortar were used to mix the mixture thoroughly. Hot pressing of the composite powder was carried out in the following range, temperature (300- 500^{0}C) and force (150- 375 Kg/cm^2) for the duration of 2 h to 4 h. Hot pressing of nanoparticles results in dense pellet whose theoretical density varies from 94% to 97%.

Preparation of nanocomposite B:

The obtained pellet B was crushed into powder and mixed with bulk bismuth antimony telluride in different weight percentage of nano and bulk e.g 50: 50, 60: 40, 70: 30. Pestle and mortar were used to mix the mixture thoroughly. Hot pressing of the composite powder was carried out in the following range, temperature (300- 500^{0}C) and force (150- 375 Kg/cm^2) for the duration of 30 min to 4 h.

RESULTS & DISCUSSION

The morphology of the pellet obtained from pure nanoparticles and nanocomposite was characterized by SEM (See Fig. 1 and2), while XRD is used to check phase purity of the nanoparticles (Fig. 3). SEM images showed nanostructured sheets with dimensions in the range of 50 – 150 nm. It is seen that nanostructured sheets of BiSbTe are in intimate contact with the bulk particle, thereby decreasing the long range order seen in the case of nanoparticles.

The transport properties (thermal conductivity, electrical conductivity, Seebeck) of these pellets were measured to evaluate ZT of the p-type bismuth antimony telluride nano composite. Thermal conductivity of the pellet was measured by hotdisk, while electrical conductivity by Jandel four probe technique. MMR (Micro Miniature Refrigerators) Seebeck instrument was used for the measurement of Seebeck coefficient. At room temperature thermal conductivity values lie between 0.80 – 0.99 W/mk, while electrical conductivity values vary from 511-823 S/cm, depending on the composition of the samples. Room temperature Seebeck coefficients (Fig. 4) of the samples are 236µV/K and 273 µV/K. The transport properties of the samples are summarized in Table 1 and Table 2. The thermoelectric transport properties of the pellet obtained from pure nanoparticles were thus characterized. The measured thermal conductivity values are between 0.86-0.89 W/mK, while, room temperature electrical conductivity lie between 290-354 S/cm. Room temperature Seebeck coefficients of the samples are in the range of 290-310 µV/K.
Figure 5 indicates that when percentage of nano: bulk ratio varies from 70-80, there is no significant change of electrical conductivity and power factor. These observations agree with Seebeck coefficient but reverse for figure of merit (ZT). It can be concluded that the ZT value attains maximum at the position of nano to bulk ratio 80 **:** 20. Thermal conductivity of P-type BiSbTe nano-composite, as prepared from nano powders with bulk commercial powder, reaches maximum for pure bulk and attains minimum when nano to bulk ratio is 90:10. Accordingly, for

higher Seebeck Cofficent, Figure of merit (ZT) values decrease slightly in the range nano to bulk ratio 90:10 as compared to nano to bulk ratio 80:20 [22-25].

The figure of merit (ZT) for nano composite, made from crashed pre-press pellets of nano powder and bulk commercial powders , shows maximum when nano to bulk 90:10 which obey same pattern as in Fig. 5.

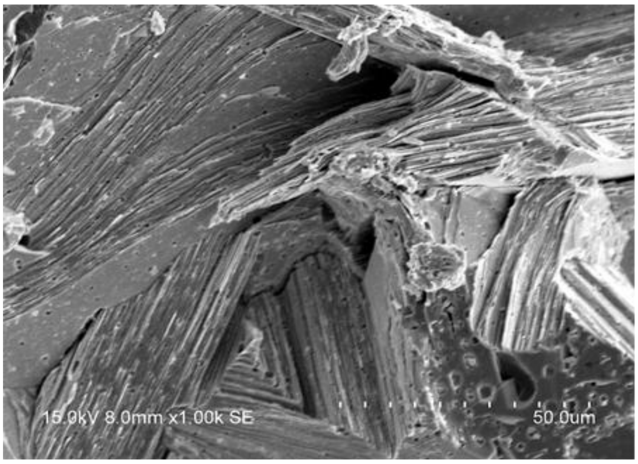
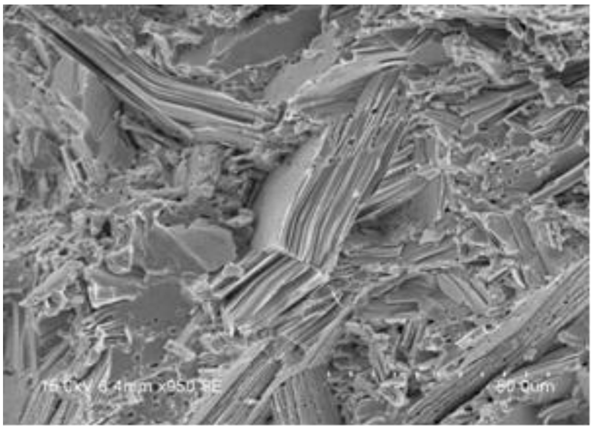


Fig. 1: Low magnification SEM image obtained from hot press bismuth antimony telluride nanoparticles.



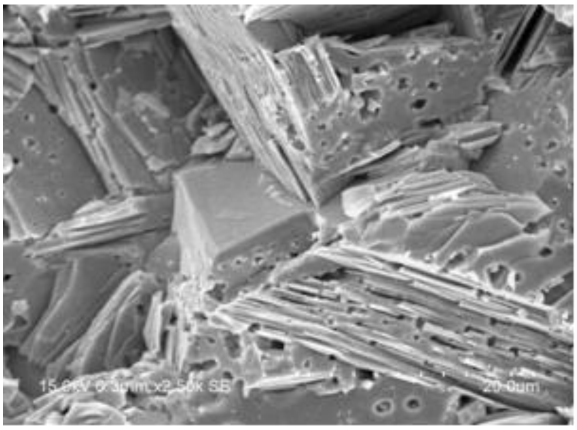


Fig. 2(a) **Fig. 2(b).**

Fig.2. Low (a) and high(b) magnification SEM images of hot pressed nanocomposite bismuth antimony telluride.

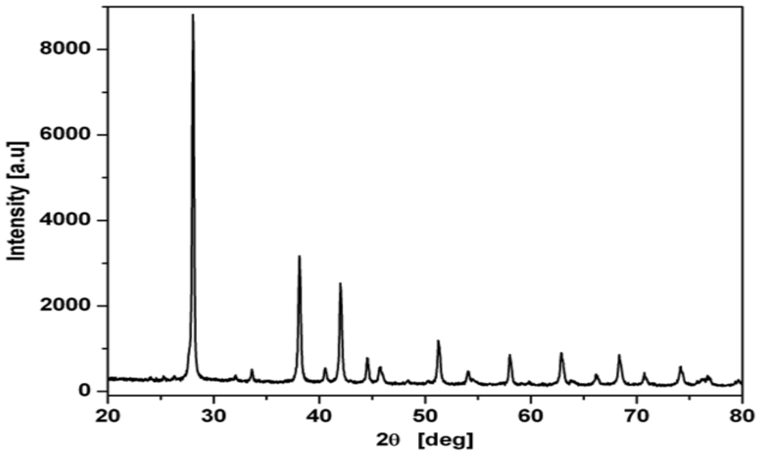


Fig. 3: XRD of nano composite obtained from hot pressed sample shows pure bismuth antimony telluride phase

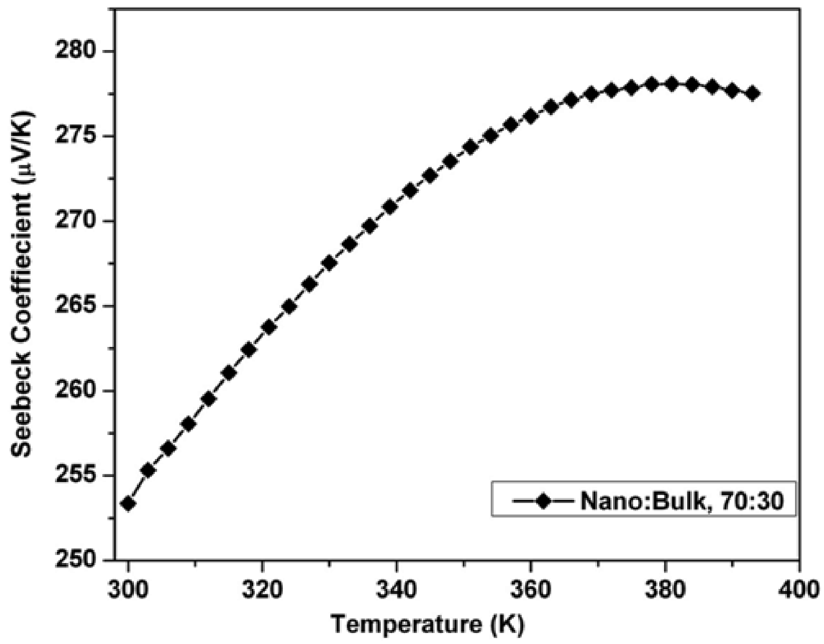


Fig. 4: Temperature dependent Seebeck coefficient of nanocomposite with nano to bulk ratio of 70:30

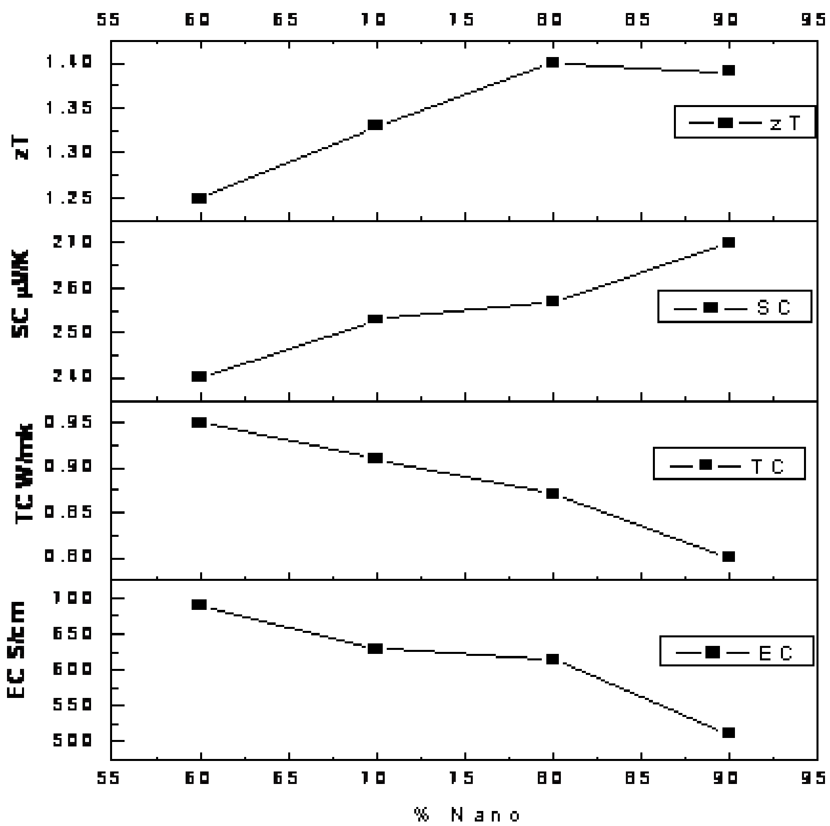


Fig. 5: Graph showing Electrical conductivity (EC), Thermal conductivity (TC), Seebeck coefficient (SC) and ZT for Nano composite (all data are recorded at room temperature).

Table 1

Composition Nano:Bulk	Electrical conductivity (S/cm)	Power factor	Thermal conductivity (W/mk)	Seebeck coefficent (μV)	ZT
100: 0	338	0.003227	0.86	309	1.14
0: 100	1094	0.004246	1.12	197	1.14
60:40	690	0.003974	0.95	240	1.26
70:30	629	0.004026	0.91	253	1.33
80:20	615	0.004062	0.87	257	1.40
90:10	511	0.003725	0.80	270	1.39

Table 1 shows thermoelectric properties of nanocomposite made from as-prepared nano powders with bulk commercial powder.

Table 2

Composition Nano:Bulk	Electrical conductivity (S/cm)	Power factor	Thermal conductivity (W/mk)	Seebeck coefficent (μV)	ZT
50:50	823	0.004584	0.99	236	1.39
60:40	727	0.004617	0.98	252	1.41
90:10	600	0.004472	0.89	273	1.51

Table 2 shows nanocomposite made from crushed pre-press pellet of nanopowder and bulk commercial powder.

CONCLUSION

We reported very high ZT compared to the reported value of ZT for conventional bulk and composite thermoelectric materials. ZT of the p-type materials at room temperature is in the range 0.5- 1.1, while in case of our nanocomposite materials room temperature ZT is in the range 1.26 -1.51 , which depends on the nano to bulk ratio. In earlier cases nanocomposite thermoelectric materials only 15 weight percent of nano was added into the bulk matrix but we have added 50 to 90 weight percentage of nano into the bulk matrix [26]. Addition of more nano leads to reduction of thermal conductivity compared to the reported nanocomposite by10-20%. In our work ZT increases with reduction of thermal conductivity of nanocomposite whereas in some reported work the overall ZT decreases with reduction in thermal conductivity [27].

ACKNOWLEDGEMENT

One of the authors, S. Chakrabarty is thankful to Dr. Arup Purkayastha for instrumental analysis and also to Dr. Sambhunath Rakshit, Principal, Government Degree College Dharmanagar for allowing to carry out the research work in the Department of Chemistry, Government Degree College , Dharmanagar. One of the author thanks UGC-NERO, Guwahati, Assam for sanctioning MRP.

REFERENCES

[1] T. M. Tritt and M. A. Subramanian, MRS Bull. 31 (2006) 188-194.
[2] J. Yang and T. Caillat, MRS Bull. 31 (2006) 224-229.
[3] C. Han, Q. Sun, Z. Li, and S. X. Dou, Adv. Energy Mater. 2016, 1600498.
[4] M. Saleemi, M. S. Toprak, S. H. Li, M. Johnsson and M. Muhammed, J. Mater. Chem. 22 (2012) 725-730.

[5] J. P. Fu, S. Y. Song, X. G. Zhang, F. Cao, L. Zhou, X. Y. Li and H. J. Zhang, CrystEngComm 14 (2012) 2159-2165
[6] K. Biswas, J. Q. He, I. D. Blum, C. I. Blum, C. I. Wu, T. P. Hogan, D. N. Seidman , V. P. Dravid and M. G. Kanatzidis, Nature 489 (2012) 414-418.
[7] T. Zhang, J. Jiang. Y. Xiao, Y. Zhai, S. Yang and G. Xu, , J. Mater. Chem. A 1 (2013) 966-969
[8] G. Chen, A. Shakouri, J. Heat Transfer, 124 (2002) 242-252.
[9] G. Chen, M. S. Dresselhaus, G. Dresselhaus, J. P. Fleurial, T. Caillat, Int. Mater. Rev. 48 (2003) 45-66.
[10] M. S. Dresselhaus, G. Chen, M. Y. Tang, R. Yang, H. Lee, D. Wang, Z. Ren, J-P. Fleurial, Adv. Mater. 19 (2007) 1043-1053.
[11] H-S. Kim, K-H. Lee, S-M. Lee, E-S. Lee, S- S. Lee, X. Li, *US 2011/0100409 A1*
[12] A. Purkayastha, S. Kim, D. D. Gandhi, P. G. Ganesan, T. B-Tasciuc, and G. Ramanath, Adv. Mater. 18 (2006) 2958-2963.
[13] S. R. Hostler, Y, Q, Qu, M, T. Demko, A. R. Abramson, X. Qiu, and C. Burda, Superlatt. Microstruct. 43 (2008), 195-207.
[14] X. Guo, X. Jia, K. Jie, H. Sun, Y. Zhang, B. Sun, H. Ma, CrystEngComm. 15 (2013) 7236-7242.
[15] H. Kim, J. K. Lee, S-D, Park, B. Ryu, J. E .Lee, B-S. Kim, B-K. Min, S-J. Joo, H-W. Lee, Y-R. Cho, Electron Mater Lett. 12 (2016) 290-295.
[16] S. Hwang, S-II. Kim, K. Ahn, J.W. Roh, D-J. Yang, S-M. Lee, K-H. Lee, J. Electron. Mater, 42 (2013) 1411-1416.
[17] B. Poudel, Q. Hao, Y. Ma, Y. Lan, A. Minnich, B. Yu, X. Yan, D. Wang, A. Muto, D. Vashaee, X. Chen, J. Liu, M. S. Dresselhaus, G. Chen, Z. Ren, Science , 320 (2008) 634-638.
[18] K. Biswas , J. He, Q. Zhang, G. Wang, C. Uher, V. P. Dravid , M. G. Kanatzidis, Nat.Chem. , 3 (2011) 160-166.
[19] W. Xie, X. Tang, Y. Yan, Q. Zhang, T. M. Tritt, J. Appl. Phys. , 105 (2009) 113713.
[20] Y. Zheng , Q. Zhang , X. Su, H. Xie , S. Shu , T. Chen ,G. Tan , Y. Yan , X. Tang, C Uher , and G. J. Snyder, Adv. Energy Mater.140 (2014) 1401391.
[21] R. J. Mehta, Y. Zhang, C. Karthik, B. Singh, R.W. Siegel,T. B-Tasciuc, G. Ramanath, Nat. Mater. , 11 (2012) 233-240.
[22] J. Chen, T. Sun, D.H. Sim, H. Peng, H. Wang, S.Fan, H. H. Hng, J. Ma, F. Y. C. Boey, S. Li. M. K. Samam, G. C. K. Chen, X. Chen, T. Wu and Q. Yan, Chem. Mater. , 22 (2010) 3086-3092.
[23] Q. Jiang, H. Yan, J. Khaliq, H. Ning, S. Grasso, K. Simpson, and M. J. Reece, J. Mater. Chem. A ,2(2014) 5785-5790.
[24] G. Carotenuto, C. L. Hison, F. Capezzuto, M. Palomba, P. Perlo and P. Conte, J. Nanopart Res.11(2009) 1729-1738.
[25] A. Purkayastha, Q. Yan, D. D. Gandhi, H. Li, and G. Pattanaik, Chem. Mater. 20 (2008) 4791-4793.
[26] X. B. Zhao, X. H. Ji, Y. H. Zhang, T. J. Zhu, J. P. Tu, and X. B. Zhang, Appl. Phys. Lett. ,86 (2005) 062111.
[27] N. Gothard, X. Ji, J. He, T. M. Tritt, J. Appl. Phys. , 103 (2008) 504314.