Aerogel Derived Nanostructured Thermoelectric Materials

FINAL REPORT

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by

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Executive Summary

Refrigeration, air conditioning, and other cooling requirements in the buildings, industry, and transportation sectors account for about 10 quads of U.S. primary energy consumption. Since the efficiency of the best Vapor Compression Cycle (VCC) systems may be approaching asymptotic values, the potential for significant improvement of current technologies may be limited. Therefore, the Department of Energy is interested in developing advanced technologies for space cooling in buildings and vehicles – as well as for refrigeration in residential, commercial, and industrial applications – that are more energy efficient, that avoid net direct greenhouse gas emissions, reduce lifecycle costs, and can impact large markets.

The efficiency of thermoelectric (TE) devices has remained frustratingly low until recently. However, new results suggest that as the length scale decreases so that the number of atoms in any direction (x , y , or z) becomes less than ca. 10^2 , quantum-confinement effects arise. This decrease in the dimensionality of the material, introduces a new ‘length scale’ variable which can be used to control the material properties which allows the investigation of new approaches that could potentially improve the efficiency of TE materials.

During this Phase I SBIR project, Aspen Aerogels investigated the feasibility of increasing the figure of merit (ZT) of TE materials by lowering the thermal conductivity and reducing the dimensionality of TE materials by preparing nanostructured TE aerogels as a new approach to develop advanced cooling technologies. The nanometer size of particles that make up the structure of the TE aerogels self assemble to form hyperbranched nanostructured aerogels of the thermoelectric materials with intrinsically low thermal conductivities.

Aspen Aerogels successfully demonstrated the feasibility of the proposed approach by preparing the first known Bi_2Te_3 hyperbranched nanostructured aerogels and determining their thermoelectric properties. Two approaches were developed during the Phase I effort to prepare the Bi_2Te_3 aerogels. Small quantities of a Bi_2Te_3 aerogel were first prepared by a two step method. To make larger quantities of Bi_2Te_3 , the two step method was simplified to synthesize the Bi_2Te_3 gels in one step to make monolithic aerogels. The project resulted in the preparation of the first Bi_2Te_3 aerogels and demonstrated that monolithic telluride aerogels can be prepared.

The thermoelectric properties of the aerogels were determined, and the Seebeck coefficients and conductivities of the hot pressed Bi_2Te_3 aerogels were similar to those published for Bi_2Te_3 nanoparticles. The thermal conductivities were not determined, so we did not demonstrate that the approach reduced the figure of merit. However, the Phase I results were very encouraging and demonstrated that aerogels of thermoelectric materials can be prepared by sol-gel methods. The methods developed provided further insight into the approaches used to prepare other nanostructured thermoelectric and chalcogenide aerogels and will lead to advanced materials and technologies for developing thermoelectric cooling in buildings, and for refrigeration in residential, commercial, and industrial applications. These new solid state TE cooling devices will have a huge impact on the environment and will reduce energy consumed in conditioning residential and industrial buildings.

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1 Introduction

Refrigeration, air conditioning, and other cooling requirements in the buildings, industry, and transportation sectors account for about 10 quads of U.S. primary energy consumption. Since the efficiency of the best Vapor Compression Cycle (VCC) systems may be approaching asymptotic values, the potential for significant improvement of current technologies may be limited. Therefore, the Department of Energy is interested in developing advanced technologies for space cooling in buildings and vehicles – as well as for refrigeration in residential, commercial, and industrial applications – that are more energy efficient, that avoid net direct greenhouse gas emissions, reduce lifecycle costs, and can impact large markets. To meet this recognized need, Aspen Aerogels developed thermoelectric materials that could improve efficiency while avoiding refrigerants that increase the threat of global warming.

The efficiency of thermoelectric (TE) devices has remained frustratingly low until recently. However, new results suggest that as the length scale decreases so that the number of atoms in any direction (x , y , or z) becomes less than $ca. 10^2$, quantum-confinement effects arise which allows additional opportunities to improve the efficiency of TE materials. This decrease in the dimensionality of the material, introduces a new ‘length scale’ variable which can be used to control the material properties. For example, as the dimensionality is decreased from 3D crystalline solids to 2D (quantum wells) to 1D (quantum wires) and finally to 0D (quantum dots), new physical phenomena are also introduced, and these phenomena may also create new opportunities to improve the efficiency of thermoelectric materials.

To develop advanced cooling technologies, Aspen Aerogels investigated increasing the figure of merit (ZT) of TE materials by lowering the thermal conductivity and reducing the dimensionality of TE materials by making nanostructured TE aerogels. The nanometer size of particles that make up the structure of the TE aerogels self assemble to form hyperbranched nanostructured aerogels of the thermoelectric materials with intrinsically low thermal conductivities. Because aerogels are also known to sinter easily, thermal treatments will be used to control the porosity, interconnectivity and thermoelectric properties of the TE aerogels.

Figure 1. Concept for nanostructured aerogel derived TE.

2 Program Objectives

The primary objective of the proposed Phase I program was to demonstrate the feasibility of preparing a hyperbranched nanostructured aerogel thermoelectric material that has an improved figure of merit over current bulk materials. We succeeded in preparing the Bi_2Te_3 hyperbranched nanostructured aerogels during the Phase I effort. The specific technical objectives were:

1. Define requirements for aerogels that would be used in TE cooling devices.
2. Synthesize a Bi_2Te_3 and Sb_2Te_3 aerogels (both p and n type).
3. Characterize materials prepared:
 - BET surface area
 - Scanning electron microscopy (SEM) and /or transmission electron microscopy (TEM) to investigate particle size and morphology.
4. Demonstrate feasibility that the nanostructured TE aerogels enhance the figure of merit by determining:
 - Figure of merit
 - Electrical conductivity
 - Thermal conductivity
5. Perform elemental analysis to confirm the composition of the aerogels synthesized.
6. Demonstrate feasibility that the nanostructured TE aerogels can be used to fabricate cooling devices.

During Phase I, Aspen Aerogels successfully demonstrated the feasibility of the proposed approach by preparing Bi_2Te_3 (n -type) aerogels and testing their thermoelectric properties. To accomplish the proposed program, we collaborated with Stephanie Brock at Wayne State University who assisted in developing the methods used to prepare bismuth telluride and with Marlow Industries who determined the properties of the materials. We succeeded in preparing Bi_2Te_3 hyperbranched nanostructured aerogels during the Phase I effort. We also determined their thermoelectric properties, and the Phase I results were very encouraging since the Seebeck coefficients of the Bi_2Te_3 aerogels were similar to those published by Dirmyer *et. al.*¹ However, we did not have time to prepare both n and p type telluride aerogels and determine their figures of merit. Considering that the results obtained during the Phase I effort were obtained on the first Bi_2Te_3 aerogels ever prepared, the results were excellent, and now that the basic synthetic procedures have been developed, we are in a position to substantially improve the properties of these materials in future efforts.

3 Phase I Technical Results

3.1 Introduction

Although no papers have been published on the synthesis of Bi_2Te_3 aerogels, there are papers that describe methods to prepare CdS ^{2,3,4,5} and CdSe aerogels,^{6,7,8} and the general synthesis strategy developed by these authors was used to prepare Bi_2Te_3 aerogels. As illustrated in Figure 2, the first step of the published methods is to synthesize semiconductor nanoparticles using the principles of colloid chemistry. The nanoparticles are stabilized by using a protecting ligand and controlling the reaction conditions such as reaction temperature, reaction atmosphere, reaction time, etc. Gelation of the nanoparticles in the 2nd step is achieved by destabilizing the

dispersion of nanoparticles by decomposing the protecting ligand by adding H₂O₂ or tetranitromethane to the dispersion. Finally aerogels of the targeted materials are obtained after aging, rinsing and supercritical drying the gels.

Figure 2. Aspen Aerogels' Bi₂Te₃ aerogels one-step synthesis strategy versus the traditional two-step literature method.

During the Phase I effort, we collaborated with Stephanie Brock at Wayne State University in developing the method to synthesize the aerogel. The usual synthetic approach is to control the growth of the nanoparticles and isolate them prior to gelation. Aspen's strategy, as indicated in Figure 2, was to skip the nanoparticle isolation step to make the aerogel preparation process easier to scale-up and more economical.

Although the synthesis of the Bi₂Te₃ gels has not been reported, there are papers on the synthesis of Bi₂Te₃ nanoparticles,^{1,9,10,11} Bi₂Te₃ nanofiber, Bi₂Te₃ powder¹² and Bi₂Te₃ crystals.¹³ The synthesis method of V-VI semiconductor nanoparticles in Reference 9 is similar to those high temperature synthesis methods for CdSe nanoparticle and aerogels reported by Brock's group. Both groups ran their reactions at 100 °C to 250 °C under inert gas atmosphere in order to obtain crystalline Bi₂Te₃ or CdSe nanoparticles. In Aspen's single-step, one-pot synthesis strategy, there is no need to isolate the Bi₂Te₃ nanoparticles; therefore, the reaction can be run at temperatures below 100 °C or even at room temperature.

3.2 Synthesis and characterization of Bi₂Te₃ aerogels prepared by the two-step method

Bismuth neodecanate, bismuth (III) triacetate (Bi(OAc)₃), bismuth (III) trichloride (BiCl₃), tellurium powder (Te), trioctylphosphine (TOP), 4-fluorothiophenol (FTP), dodecanethiol, acetone, heptane, dimethylacetamide (DMAC), triethylamine (TEA), diphenyl ether, toluene, and ethanol (EtOH) were obtained from Sigma-Aldrich and were used as received.

The experimental procedure employed to synthesize the Bi_2Te_3 nanoparticles involved heating the bismuth neodecanoate and diphenyl ether in a flask to 150 °C followed by addition of dodecanethiol (the thiol capping agent) to the reaction mixture. After stirring the reaction mixture for 30 min, tellurium (Te) dissolved in trioctylphosphine (TOP) was injected into the solution and the yellow solution turned black as the Bi_2Te_3 formed. After a reaction time of 1 h, the thiol capped Bi_2Te_3 was isolated by adding toluene and centrifuging. The thiol capped nanoparticles were dispersed in acetone and the wet gel was formed by oxidizing thiolate groups (dodecanethiol) by treating them with tetranitromethane (TNM), and finally, the gels were dried using supercritical CO_2 to form the aerogels.

The morphology of Bi_2Te_3 nanoparticles and aerogels was determined by transmission electron microscopy (TEM), and the corresponding elemental composition was determined by energy dispersive spectroscopy (EDS). The nanoparticles obtained after a growth time of 1 h show 20-30 nm diameter agglomerates of needle shaped particles (Figure 3a). Figure 3b shows the TEM of the aerogel prepared from the corresponding nanoparticles shown in Figure 3a. The aerogels displayed a colloidal morphology consisting of an interconnected hyperbranched network of nanoparticles.

Figure 4 and Figure 5 show the elemental composition of the nanoparticles and aerogels by Energy Dispersive Spectroscopy (EDS) conducted in the TEM instrument. Integration of the EDS results indicated that the Bi:Te:S ratio was 2:2.96:1.24 for the nanoparticles, corresponding to nearly stoichiometric Bi_2Te_3 ($\text{Bi}_2\text{Te}_{2.96}\text{S}_{1.24}$) with the sulfur content attributed to thiolates bonded to the surface of the nanoparticles. The aerogel had a Bi:Te:S ratio of 2:2.6:0.4, suggesting some Te is lost during redispersion and gelation of the nanoparticles and supercritical extraction of the gel to form the aerogel, yielding a slightly Bi-rich phase $\text{Bi}_2\text{Te}_{2.67}\text{S}_{0.38}$. The decrease in sulfur content is indicative of loss of thiolate capping ligands bonded to the nanoparticles and is consistent with decomposition and removal of the thiolates by the oxidative gelation mechanism.

Figure 3: TEM images of (a) Bi_2Te_3 nanoparticles and (b) Bi_2Te_3 aerogel.

Figure 4. EDS of Bi₂Te₃ nanoparticles.

Figure 5. EDS of a Bi₂Te₃ aerogel.

The powder X-ray diffraction (XRD) pattern of the as synthesized nanoparticles and the corresponding aerogel (Figure 6) was found to match with the powder diffraction file of Bi₂Te₃-

PDF#15-0863 indicating tellurobismuthate phase. No other peaks were observed, suggesting the samples are relatively pure.

Figure 6. Powder XRD of Bi_2Te_3 nanoparticles and corresponding aerogel.

Nitrogen adsorption/desorption isotherms were acquired to determine the surface area and porosity characteristics of the Bi_2Te_3 aerogels after samples were heated in vacuum at 100 °C for 24 h to remove any moisture or volatile impurities from the surface of the aerogels (Figure 7). The adsorption/desorption isotherms illustrated in Figure 7 indicates that the aerogel display a type II or IV isotherm curve and the BJH pore size distribution extends beyond the macropore region (>100 nm). Type II and IV isotherms are indicative of nonporous adsorbents or adsorbents having relatively large pores. The Bi_2Te_3 aerogel has low porosity since the desorption isotherm essentially retraces the adsorption isotherm.

Figure 7. Nitrogen adsorption (black filled squares)/desorption (green filled circles) isotherm for aerogel obtained from Bi_2Te_3 nanoparticles.

The Brunauer, Emmet and Teller (BET) surface area was 40 m²/g. Based on this surface area, the calculated average spherical particle diameter is approximately 20nm. The desorption average pore size calculated using the Barret, Joyner and Halenda (BJH) model (4V/A) was 10 nm and the cumulative pore volume 0.18 cm³/g. The relatively low surface area is attributed in part to the crystallinity and high density of Bi₂Te₃ particles; when normalized for the density differences between silica and bismuth telluride, this surface area corresponds to a surface area of over 150 m²/g for a comparable silica aerogel.

Figure 8. The BJH pore size distribution for the aerogels.

In order to ensure good electrical conductivity between particles, the organic ligands bonded to the surface of the particles need to be removed, since these organic groups would create an insulating barrier at the interface between particles. In order to remove these organic groups, the Bi₂Te₃ aerogel was heated under a flowing argon atmosphere. Infrared spectroscopy (IR) was used to probe the removal of organic groups from the surface of the Bi₂Te₃ aerogel network, and Figure 9a and b show the IR spectra of Bi₂Te₃ aerogel before and after heating the aerogels in the furnace at 200 °C under an atmosphere of flowing Ar. The absence of peaks at 2918 cm⁻¹ and 3140 cm⁻¹ (aliphatic C-H stretches) in Figure 9b indicates that the heat treatment removed the organic ligands from the surface of the Bi₂Te₃ aerogel.

Figure 9. IR of Bi₂Te₃ aerogel (a) before and (b) after heating under Ar in a flow furnace at 200 °C.

Powder XRD was employed to determine whether the tellurobismuthite crystalline phase observed for the nanoparticles was retained or different or additional phases formed upon preparation of the aerogel. Figure 10 shows the powder XRD of the Bi_2Te_3 aerogel before and after heating the aerogel in a furnace under a flowing Ar atmosphere at 200 °C. The powder XRD pattern sharpened after heating, suggesting an increase in crystallite size, but the Bi_2Te_3 tellurobismuthite phase was preserved. The line diagram included in Figure 10 corresponds to the PDF # 15-0863 of Bi_2Te_3 .

Figure 10. Powder XRD of Bi_2Te_3 gel before and after heating in furnace under Ar at 200 °C.

3.3 Preparation of Bi_2Te_3 aerogels by the one-step method

To scale-up the synthesis of Bi_2Te_3 aerogels our objective was to develop a one step procedure by skipping the step involving the isolation of the nanoparticles. We used the same Te source as previously described so the first step was to dissolve tellurium powder in TOP to form a TOP-Te complex. We replaced bismuth neodecanoate with an alternative precursor and alternative solvents after investigating the solubility of the new precursors in various potential solvents. As one example, bismuth (III) triacetate was dissolved in DMAc and then the desired ratio of 4-fluorothiophenol (FTP) was added. After the solution turned red, the Te-TOP solution was rapidly added, and the solution turned black. The solution was poured into molds and placed in a furnace set at 60-70 °C for gelation. Gel times ranged between 12 and 24 hrs depending on the concentration and the amount of FTP in the system. The solvent and residual reactants within the gel were exchanged with ethanol prior to supercritical drying.

During this Phase I effort, we studied the effect of reaction conditions on the properties of the aerogels. The key step in Bi_2Te_3 aerogel synthesis is the formation of Bi_2Te_3 wet gels, and the gelation of Bi_2Te_3 sols are influenced by the FTP/Bi ratio, Bi and Te concentrations, solvent, and reaction temperature. The reaction temperature was room temperature for most preparations and

the aerogels obtained were amorphous. However, we obtained crystalline Bi_2Te_3 aerogels when the reaction temperature was increased to 60-70 °C. The Bi_2Te_3 aerogels were post heat-treated to remove residual organic material before the thermoelectric properties were tested. The aerogels were characterized by XRD, nitrogen adsorption, SEM, FTIR and elemental analysis.

After the formation of Bi_2Te_3 gels, the gels were aged to strengthen them and the solvent was exchanged with ethanol prior to supercritical drying. If the gels were exposed to air, the surface of the gels turned white due to oxidation of Bi_2Te_3 . During the aging process, the gels became stronger and shrank expelling clear solvent. If the container was not well sealed, the liquid evaporated and the Bi_2Te_3 gels were easily oxidized when exposed directly to air. Examples of the gels prepared are illustrated in Figure 11. The gels in Figure 10 are covered with ethanol to exchange the reaction solvent with ethanol before they are supercritically dried.

Figure 11. Photos of gels from WD-172-14B, C and D.

The aerogels were characterized by SEM to study their microstructures. SEMs of the surface of a typical aerogels are shown in Figure 12.

Figure 12. SEMs of samples WD-172-9A and WD-172-16B at 10K magnification.

The FTP/Bi molar ratio plays a very important role in the formation of Bi_2Te_3 aerogels since it is a capping ligand for Bi to prevent particle growth and Bi_2Te_3 particles from agglomerating. Therefore, we expected to see some differences in the microstructures of the aerogels prepared with different FTP/Bi molar ratios. The FTP/Bi ratio used in the preparation of WD-172-9A and 16B were 3.5 and 8.5, respectively. The SEM images of these two samples are shown in Figure

13. The most obvious difference between the two aerogels is that the one made with FTP/Bi ratio of 8.5 has smaller Bi_2Te_3 particles than the one with a FTP/Bi ratio of 3.5. Aerogel WD-172-9A contains primary spherical particle that are ~ 20 nm or less, and aerogel WD-172-16B which was prepared with FTP/Bi ratio of 8.5, is composed of primary particles smaller than 10 nm. Pores with sizes >100 nm are also observed in all the aerogels. These SEMs indicate that the Bi_2Te_3 aerogels are composed of interconnecting spherical Bi_2Te_3 nanoparticles and the primary particle size can be controlled by adjusting the FTP/Bi ratio.

Figure 13. SEM of a) WD-172-9A and b) WD-172-16B at 100K magnification.

XRD was used to determine the crystallinity Bi_2Te_3 aerogels and to determine phases present. The XRD pattern of Sample WD-172-9D is shown in Figure 14. One can see a broad peak near $2\theta = 28^\circ$ which is near that of the most intense diffraction peak of Bi_2Te_3 . A secondary broad peak is observed near 52° . All samples prepared either under basic conditions (WD-172-6A, C and D) or acidic conditions (WD-9C and 9D) had similar X-ray diffraction patterns and were considered to be amorphous or at best weakly crystalline.

Figure 14. Powder XRD pattern for the Bi_2Te_3 particles from WD-172-9D.

3.3.1 Effect of heat-treatment on crystallinity

As one can see from the XRD pattern discussed above, the crystallinity of the product is poor for products prepared at room temperature and in order to increase crystallinity, we prepared gels at

higher reaction temperatures and also heat treated the samples under a nitrogen atmosphere. The X-ray diffraction pattern for a sample prepared at 70 °C (WD-172-20-70C) and that of the reference diffraction pattern PDF 15-0683 are shown in Figure 15. We expected to obtain amorphous Bi_2Te_3 but obtained a crystalline Bi_2Te_3 aerogel at reaction temperatures of 70 °C.

The WD-172-20 aerogel was heated at 250, 350 and 480 °C and X-ray diffraction patterns determined. Analysis of the data indicated that all samples were highly crystalline after heat treatment. Tellurobismuthite (PDF 15-0683) was the only crystalline phase observed in samples WD-172-20-70C and WD-172-20-250C. The samples heated to higher temperatures also contained an oxide phase (Bi_2TeO_5 , smirnite: PDF 24-0154) indicating that any oxidation of the samples will lead to crystallization of the oxide phase when heated to temperatures above 350 °C.

Figure 15. XRD of Bi_2Te_3 aerogel prepared at 70 °C.

Figure 16. XRD pattern of WD-172-20 after heating at 480 °C.

The SEM images in Figure 17 show the microstructure of Bi_2Te_3 aerogels prepared at 70 °C (WD-172-20). The network of Bi_2Te_3 aerogel in WD-172-20 is composed of interconnected particles with varying particle sizes and shapes. The particles are cylindrical with length of ~80 nm and width of 10-20 nm.

Figure 17. SEM image of WD-172-20-70 °C at (a) 10K and (b) 100K magnification.

The SEM images in Figure 18 show the microstructure of Bi_2Te_3 aerogels (WD-172-20) after heat-treatment under nitrogen at 250 °C and 350 °C, respectively. Comparing the SEMs of Bi_2Te_3 aerogels without heat-treatment (WD-172-20, Figure 17), one can see that the most obvious difference is that the structure for Bi_2Te_3 aerogels heat-treated at 250 °C and 350 °C is much coarser than those of Bi_2Te_3 aerogels without heat-treatment. For Bi_2Te_3 aerogels heat-treated at 250 °C and 350 °C, the porous network of Bi_2Te_3 aerogel was composed of interconnected particles with varying particle sizes and shapes: on the surface of the aerogel, the particles were cylindrical with lengths up to 150 nm and widths of ~20 nm or more. Since heat treatments increase the particle size, heat-temperatures below 250 °C in nitrogen are preferred because heating at higher temperatures will lead to a significant increase in the particle sizes.

Figure 18. SEMs of a) WD-172-20-250C and b) WD-172-20-350 °C.

3.3.2 Effect of FTP/Bi molar ratio on nitrogen adsorption and BET surface areas

The adsorption and desorption isotherms and the corresponding pore size distribution of Bi₂Te₃ aerogels with FTP/Bi molar ratios of 3.5 (WD-172-9A) and 8.5 (WD-172-16B) are shown in Figure 19 and Figure 20. The shape of the isotherms of Bi₂Te₃ aerogels is similar to that of the Bi₂Te₃ aerogel shown in Figure 7 except in this case the desorption isotherm does not retrace the adsorption isotherm indicating these aerogels contain more mesopores. The adsorption/desorption isotherms for Bi₂Te₃ aerogels represent a type IV curve, which is characteristic for mesoporous materials with pore diameter in the range of 2-100 nm. However, there is a sharp up-turn on the isotherms in the high relative pressure region (P/P_0 close to 1), which is similar to the Type II isotherms for monolayer adsorption on nonporous material. The sharp up-turn indicates lack of saturation at high pressure, which is caused by the liquid condensation associated with the presence of macroporous with pore size larger than 50 nm in the Bi₂Te₃ aerogels. The presence of macropores can be seen in the SEM microphotographs (Figure 13).

The data listed in Table 1 indicates that the surface areas for Bi₂Te₃ aerogels depend on the FTP/Bi ratio. The maximum surface areas (the smallest particles) were obtained for FTP/Bi ratios of around 8. The lowest surface was for sample WD-172-20 which was crystalline according to the XRD results and contains larger particles according to the SEMs (Figure 17). The surface areas of Bi₂Te₃ aerogels with FTP/Bi ratio of 2 and 12.5 were 55-67 m²/g, which is lower than those with FTP/Bi ratio of 6.25 and 10, as one can see from Figure 21. Accordingly, the average pore volume of Bi₂Te₃ aerogels with FTP/Bi ratio of 6.25 and 10 are also higher than those with FTP/Bi ratio of 2 and 12.5. These results indicate that low (such as 2) or high (such as 12.5) FTP/Bi ratios lead to lower surface areas for Bi₂Te₃ aerogels.

Table 1. Surface areas, pore volumes and average pore diameters of Bi₂Te₃ aerogels.

Sample ID	Reaction or heat treatment temp. (C)	FTP/Bi molar ratio	BET surface area (m ² /g)	Calc. ave. particle diameter (nm)	BJH Desorption cumulative pore volume (cm ³ /g)	BJH Desorption average pore diameter (4V/A), (nm)
WD-172-9A	RT	3.5	77.1	9.9	0.21	11.2
WD-172-9B	RT	5	75.2	10.4	0.20	11.1
WD-172-14A1	RT	6.25	83.1	9.4	0.25	12.7
WD-172-14B1	RT	7.5	72.2	10.6	0.18	10.7
WD-172-14C1	RT	10	78.3	9.9	0.25	12.6
WD-172-14C2	60	10	62.5	12.5	0.16	10.7
WD-172-14D1	RT	12.5	66.1	11.9	0.15	9.8
WD-172-14D2	60	12.5	68.0	11.5	0.17	11.1
WD-172-16A+1	70	7.5	91.3	8.5	0.19	9.0
WD-172-16B1	70	8.5	91.9	8.5	0.22	9.7
WD-172-17A	70	6.25	78.4	9.9	0.17	9.3
WD-172-20A	70	8.5	41.6	18.5	0.09	9.5
WD-172-20-250	250	8.5	17.9	41.5	0.04	13.8
WD-172-20-350	350	8.5	9.4	82.5	0.02	11.8
WD-172-21A	70	2	54.5	14.5	0.13	10.8

Figure 19. Adsorption and desorption isotherms of WD-172-9A (FTP/Bi = 3.5) and WD-172-16B (FTP/Bi = 8.5) Bi_2Te_3 aerogels.

Figure 20. Pore size distributions for WD-172-9A (FTP/Bi = 3.5) and WD-172-16B (FTP/Bi = 8.5).

Figure 21. Effect of FPT/Bi ratio on the BET surface area.

The adsorption and desorption isotherms and the corresponding pore size distributions after heat treatment at 250 and 350 °C are shown in Figure 22 and Figure 23. One can see that the adsorbed nitrogen volume decreased as the heat treatment temperature increased. The decrease in surface area was also dramatic as indicated in Table 1. The surface area for heat-treated sample at 250 °C is only half of the surface area for sample without heat treatment and the surface area for sample heat treated at 350 °C is ~9 m²/g. Therefore, heat-treatment increases crystallinity but decreases the surface area as the particle sizes increase due to crystallization and particle coarsening.

Figure 22. Adsorption and desorption isotherms for WD-172-20 after heat-treatment at 250 and 350 °C under nitrogen.

Figure 23. Pore size distributions for WD-172-20 after heat-treatment temperatures under nitrogen.

3.3.3 Elemental analysis of Bi_2Te_3 aerogels

The elemental analysis results are shown in Table 2 for samples WD-172-16B1, 20 and 21B. The corresponding molar compositions for these samples are also listed. The calculated results showed that the Te/Bi molar ratios for WD-172-16B1, 20 and 21B were 1.38, 1.35 and 1.27 respectively and all of the samples are Bi rich. However, the molar ratios of Te/Bi are approaching the theoretical value of 1.5 and adjustments to the synthesis procedure are needed to increase the Bi/Te ratio which will be addressed in Phase II. The sulfur and hydrogen content for all three samples were well below the detection limits, i.e. <0.5, indicating that undetectable amounts of sulfur remain in the sample after extraction.

Table 2. Elemental analysis results for Bi_2Te_3 aerogels.

Sample ID	Bi (wt%)	Bi (mol)	Te (wt%)	Te (mol)	C (wt%)	C (mol)	Te/Bi molar ratio
WD-172-16B1	43.6	0.21	36.7	0.29	0.53	0.05	1.38
WD-172-20	47.4	0.23	39.8	0.31	0.67	0.06	1.35
WD-172-21B	45.3	0.22	35.9	0.28	0.95	0.08	1.27

3.3.4 Thermal stability of the Bi_2Te_3 aerogels

In order to remove the organics from the aerogels and reduce any oxides present, heat-treatment at 250 °C under H_2/N_2 mixture was carried out for samples submitted for determination of thermoelectric properties. Table 3 summarizes the weight loss for the samples heat treated at 250 °C and data shows that the weight losses of the materials are in the range of 3-5 wt%. This weight loss is due loss of organics or reduction of any oxides present due to oxidation of the Bi_2Te_3 upon exposure to air and moisture.

Table 3. Weight loss of Bi₂Te₃ aerogels after heat-treatment in H₂/N₂ mixture at 250 °C.

Sample ID	Target density (g/ml)	FTP/Bi molar ratio	Weight before heat-treatment (g)	Weight after heat-treatment (g)	Weight loss (wt%)
WD-172-16BA	0.10	7.5-8.5	2.00	1.90	5
WD-172-20-17BCD	0.08	7.5-10	1.99	1.92	3.5
WD-172-21A	0.10	2	2.04	1.95	4.4

3.4 Thermoelectric properties of the Bi₂Te₃ aerogels

The three samples listed in Table 3 and one from Wayne State University (WS Bi₂Te₃) were sent to Marlow Industries for characterization. Each powdered aerogel material was loaded into a 0.375" graphite die in successive layers with lightly pressing until all of the very low density material would fit into the die, and then it was then cold pressed at 1000 kg force. The loaded die was then positioned in the hot press. The press chamber was closed, evacuated and filled with nitrogen gas prior to heating. Minimal force of ~200 kg was applied during heating with the full force was applied after the temperature set point of 450 °C was reached. The first sample, WD21-A, was processed at 450 °C and 400 kg force. The physical integrity of the sample was poor so the remaining samples were processed at 450 °C and 500 kg force.

The sample WD21-A was prepared in air since it had already been exposed to air prior to shipment. However, it did not flow well during die loading, so the Wayne State University sample was prepared inside a nitrogen purged glove box. An improvement in handling and the final product appearance was observed by allowing 2-4 hours drying time before die loading in a nitrogen atmosphere. This difficulty with material flow is expected from Bi₂Te₃ exposed to room air and/or moisture.

Table 4 summarizes the test results for the best samples. These results are extremely encouraging and the Seebeck Coefficients were similar to those published by Dirmyer.¹ However, the properties are lower than those for Bi₂Te₃ bulk materials. It is likely that the effects of air and moisture exposure and the composition of the aerogel powders are the primary cause of the lower performance since the aerogel materials were exposed to air after supercritical drying. In addition, the limited number of samples prevented optimization of the hot-pressing process. For instance, it is thought that a different spacer may be necessary to improve the integrity of the pressed material. Prior to sending the samples to Marlow Industries, they were heated in a H₂/N₂ atmosphere to reduce any oxides present, but the results also indicate that this process also needs to be improved.

Table 4. Thermoelectric properties of the aerogels.

Sample	Hot press force (kg)	Resistance (mΩ)	Resistivity (mΩ-cm)	σ (S/cm)	Density (g/cm ³)	Seebeck (μV/°C)
WD21A	400	5 - 8.3	7.3 - 12.8	78-140	6.5	-107.8
WS Bi ₂ Te ₃	500	1.4	2.27	440	4.81	-117.43
Bulk Bi ₂ Te ₃ ¹¹			1.4	714	7.7	-180

3.5 Summary of results for Phase I

The primary objective of the Phase I program was to demonstrate the feasibility of preparing a hyperbranched nanostructured aerogel thermoelectric material that has an improved figure of merit over current bulk materials. We succeeded in meeting most of our objectives and prepared Bi_2Te_3 hyperbranched nanostructured aerogels during the Phase I effort. We also determined their thermoelectric properties, and the Phase I results were very encouraging since the Seebeck coefficients of the Bi_2Te_3 aerogels were similar to those published by Dirmyer *et. al*¹ who used a similar synthetic procedure to prepare Bi_2Te_3 nanoparticles. Considering that the results obtained during the Phase I effort were obtained on the first Bi_2Te_3 aerogels ever prepared, the results were excellent and the thermoelectric properties can easily be improved during the Phase II effort.

Two approaches were developed during the Phase I effort to prepare Bi_2Te_3 aerogels. We collaborated with Brock at Wayne State University during the Phase I effort, and her group successfully prepared a Bi_2Te_3 aerogel by a two step method that she has developed to prepare other chalcogenide aerogels. Aspen's synthesis strategy was to simplify the two step method, and we synthesize the Bi_2Te_3 gels in one step followed by aging, rinsing and supercritical drying. In Aspen's strategy, the formation of nanoparticles was skipped, which will make the process more economical and much easier to scale-up. The key step in Bi_2Te_3 aerogel synthesis is the formation of Bi_2Te_3 gels which was influenced by the FTP/Bi ratio, Te concentration, solvent, concentration of the precursors, and reaction conditions. For example, by adjusting the FTP/Bi ratio, we were able to control the size of the primary Bi_2Te_3 nanoparticles. The strength of the Bi_2Te_3 gels was also affected by the aging temperature, and aging time.

We overestimated how much progress we could accomplish during the Phase I effort, and we did not have time to prepare a Sb_2Te_3 aerogel or prepare $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ (*n*-type) and $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ (*p*-type) materials to optimize the Seebeck coefficient. Also, we did not have time to make additional Bi_2Te_3 aerogel samples to determine the TCs of the aerogels materials. Therefore, we could not determine the effect of the aerogel's nanostructure and lower thermal conductivity on the figure of merit. The two best hot-pressed aerogels had different densities and electrical conductivities. It is very interesting and encouraging that the lower density sample had a lower resistivity and a higher electrical conductivity than the sample with a higher density suggesting that it is feasible to prepare lower density – low thermal conductivity materials that will have a higher figure of merit. If the TC of our best Bi_2Te_3 aerogel is below $0.6\text{W/m}\cdot\text{K}$, then the ZT would be comparable to bulk Bi_2Te_3 materials ($\text{ZT} = 0.34$).¹⁴

We succeeded in demonstrating the feasibility of preparing Bi_2Te_3 aerogels, and based on our Phase I results, we believe that we can substantially improve upon the results obtained during future projects and prepare Bi_2Te_3 hyperbranched nanostructured aerogels that have superior properties to current state-of-the-art bulk Bi_2Te_3 materials.

4 Products developed under the award

We developed synthesis methods and prepared the first Bi_2Te_3 aerogel during this project.

4.1 Publications

Wenting Dong, Wendell Rhine, Greg Caggiano, Owen R. Evans, George Gould, Aspen Aerogels, Inc., Northborough, MA, John White, Jeff Sharp and Pat Gilbert, Marlow Industries, Inc., Dallas, TX, Stephanie Brock, Shreyashi Ganguli, Wayne State University, Detroit, MI , “One-step synthesis of bismuth telluride aerogels for thermal electric applications,” Materials Research Society, Aerogel Symposium, Nov 29, 2010 -Dec 3, 2010.

4.2 Collaborations

During this project, we collaborated with Stephanie Brock at Wayne State University who assisted in developing the methods used to prepare bismuth telluride. We also continued our collaboration with Marlow Industries who determined the properties of the materials.

4.3 Technologies/Techniques

We developed a new one-step method to prepare significant quantities of the first Bi₂Te₃ aerogels.

4.4 Inventions/Patent Applications

A disclosure is being prepared on the method developed to prepare Bi₂Te₃ aerogel by the one step method.

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