Thermoelectric Performance Enhancement by Surrounding Crystalline Semiconductors with Metallic Nanoparticles

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Direct conversion of thermal energy to electricity by thermoelectric (TE) devices may play a key role in future energy production and utilization. However, relatively poor performance of current TE materials has slowed development of new energy conversion applications. Recent reports have shown that the dimensionless Figure of Merit, ZT, for TE devices can be increased beyond the state-of-the-art level by nanoscale structuring of materials to reduce their thermal conductivity. New morphologically designed TE materials have been fabricated at the NASA Langley Research Center, and their characterization is underway. These newly designed materials are based on semiconductor crystal grains whose surfaces are surrounded by metallic nanoparticles. The nanoscale particles are used to tailor the thermal and electrical conduction properties for TE applications by altering the phonon and electron transport pathways. A sample of bismuth telluride decorated with metallic nanoparticles showed less thermal conductivity and twice the electrical conductivity at room temperature as compared to pure Bi$_2$Te$_3$. Apparently, electrons cross easily between semiconductor crystal grains via the intervening metallic nanoparticle bridges, but phonons are scattered at the interfacing gaps. Hence, if the interfacing gap is larger than the mean free path of the phonon, thermal energy transmission from one grain to others is reduced. Here we describe the design and analysis of these new materials that offer substantial improvements in thermoelectric performance.

**Nomenclature**

\[ ZT = \text{Dimensionless Figure of Merit, } ZT = S^2\sigma T/\kappa \]

\[ S = \text{Seebeck coefficient, } [\mu V/K] \]

\[ \sigma = \text{Electrical conductivity, } [S/m] \]

\[ \kappa = \text{Thermal conductivity, } [W/m\cdot K] \]

\[ T = \text{Absolute temperature, } [K] \]

\[ S^2\sigma = \text{Power Factor, } [W/m\cdot K^2] \]

**I. Introduction**

Thermoelectric (TE) devices are promising because of their simple energy harvesting scheme as a regenerative cycle, such as waste heat recovery and environmentally-friendly refrigeration.$^{1,2}$ Bismuth telluride,
Bi₂Te₃, and its alloys are currently the best-known materials for TE cooling devices due to their high TE performance at room temperature. However, further improvement in the TE Figure of Merit (FoM) is essential for power generation devices. It is desirable to develop materials that have high S and σ, and low κ for high FoM. Such materials are difficult to find in nature and hard to engineer. For most materials, it is difficult to alter the property of individual parameters independently, especially σ and κ: as κ is reduced, σ also is reduced. This tendency is especially prominent for metals where the Wiedemann-Franz law describes heat and electrical transport following the same trend. Since the electron and phonon properties of a given material can be tailored at the nano-scale dimensions such as quantum wells, superlattices, quantum wires, and quantum dots where quantum effects are dominant, the energy spectra of electrons and phonons can be controlled by altering the size of the structures, leading to new ways to increase the TE FoM. Recently, efforts have been made to produce new TE material designs that leverage promising nanotechnology to enhance their TE performance.

In this paper, the development of Bi₂Te₃ grains decorated with metallic nanopowders is explored as a new type of thermoelectric material. Figure 1 illustrates an aggregated form of Bi₂Te₃ in which each crystal grain is surrounded by metallic nanoparticles. This morphological arrangement shows significant performance improvement by reducing thermal conductivity (TC) from one grain to another through a separation gap greater than the phonon mean free path (MFP). At such grain boundaries, phonons scatter and contribute to a reduction of thermal conductivity κ. The separation gap is bridged by metallic nanoparticles that act as pathways between Bi₂Te₃ grains, increasing the electrical conductivity (EC) between Bi₂Te₃ grains.

Size tailoring of the Bi₂Te₃ crystals becomes critical since the overall TE FoM can be determined by the nanostructure of low-dimensional materials. The metallic nanoparticle size and their uniform dispersion over the grain surfaces are important factors influencing the reduction level of thermal conductivity by setting up phonon bottlenecks between nanoparticles where phonon scattering takes place.

![Figure 1. New material design of thermoelectric crystal](image)

To maximize its TE performance, bismuth telluride was first synthesized into a form of low-dimensional nanocrystal. Since phonon scattering depends on the size and shape of the nanoparticles, good control over these parameters is essential. Basically, nanometer-sized particles tend to aggregate due to a large surface-to-volume ratio and high surface energy. In this regard, separation and uniform dispersion of nanocrystal Ag particles in Bi₂Te₃ powders are great challenges. Ag and Bi₂Te₃ nanoparticles were dispersed using an ultrasonication process. For the ultrasonication process, distilled water was added to the nanocrystal powders. This dispersion method generates high-intensity ultrasonic waves which create transient cavitation and acoustic streaming and effectively separate nanocrystal aggregation.

II. Experimental

A. Experimental Procedure

All analytical grade chemicals were used without further purification. In a typical synthesis process, bismuth chloride (BiCl₂ >99%) and telluride (Te, 99.999%) powder were prepared for 2:3 molar ratio solution in
N,N-dimethylformamide (DMF). Potassium hydroxide (KOH) was added, and then organic surfactants [ethylenediaminetetraacetic acid disodium salt (EDTA)] were added to the bismuth telluride solution followed by mixing. The final solution was transferred to a Teflon-lined autoclave which was sealed immediately and heated to the reaction temperature of 180°C. During the reaction, the solution was stirred by a stainless steel stirrer with a rotational speed of 100 rpm. After 24 hours reaction time at 180°C, the autoclave was cooled to room temperature. The precipitated dark grey products were filtered, washed with distilled water and absolute ethanol several times, and dried in vacuum at 80°C for 24 hrs. The gold nanoparticles (20nm colloidal gold, SPI) suspended in the aqueous solution and silver nanoparticles (<150nm, 99% silver nanopowder, Sigma-Aldrich) were also prepared for mixing.

Gold colloidal and silver nanopowders with distilled water were then added to Bi$_2$Te$_3$ powder and then evaporated while being centrifuged. For further characterization of Bi$_2$Te$_3$ crystal grains with Au or Ag nanoparticles, square-shaped pellets were prepared using the hot press method in argon environment using 50 MPa in a 10mm square 15-5 stainless steel die. The powders were sealed in a graphite die and gradually heated to 200°C. After 1 hour, the mold was cooled slowly to room temperature. The metal loading levels, thermal treatment temperature, and pressure were determined after numerous different sample preparations. TE properties were found to be sensitive to changes in the individual parameters. Four samples were prepared. The amount of gold used to prepare the first, second, and third samples were 0%, 0.001%, and 0.05% of Bi$_2$Te$_3$ by weight, respectively. The amount of silver used to prepare the fourth sample was 0.05% of Bi$_2$Te$_3$ by weight.

The structural characterization of bismuth telluride nanocrystals was performed using high-resolution field emission scanning electron microscopy (FESEM, JEOL JSM-6360), field emission transmission electron microscopy (FETEM, FEI company Tecnai G2 F30), and Micro-Area X-ray diffraction (XRD, Rigaku D/MAZ-2500) with 18kW.

B. Sample holder design for TE characterization

Figure 2(a) shows the sample holder system consisting of a resistance heater with adjustable clamp. The resistance heater was used to impart a thermal pulse to the specimen. At any elevated temperature, the resistance heater created a thermal pulse that exceeded the ambient temperature. Figure 2(b) shows the sample holder that was made from a machinable ceramic tile (model #960-15, Cotronics Corp.) along with other ceramic parts. Molybdenum screws (model #4-40, Thermo Shield) were used due to a lower thermal coefficient of expansion (CTE) compared to alumina-based ceramics. One side had two S-type thermocouples made of 0.003 inch diameter wires of pure platinum and platinum/rhodium (10%) sourced from Alfa Aesar Inc. The opposite side had two ceramic rods to hold a sample in place. A small ceramic plate was screwed onto the sample holder to provide clamping pressure to the thermocouples. The sample was inserted into the holder and placed in a vacuum chamber. The chamber was then evacuated to ~1E-5 torr, and argon gas was injected twice to purge any oxygen remaining in the chamber. Seebeck coefficient, electrical conductivity, and thermal conductivity were measured at room temperature. The system developed for TE characterization used nanovoltmeters and an AC/DC current source with the LabVIEW data acquisition system.

![Figure 2. Hand-built sample holder for thermoelectric properties measurement (a) actual item with resistance heater (b) CAD drawing with dimensions in mm](image)

### III. Results and discussions

The solvothermal synthesis successfully produced dark grey powder of bismuth telluride nanocrystal after separation procedure including the filtering, washing and drying. Figure 3(a) exhibit XRD of bismuth telluride nanocrystals fabricated using KOH and EDTA. All peaks in the patterns correspond to the reflections of rhombohedral phase R 3m with lattice constants a=4.28Å and c=30.50Å, which are in agreement with the reported values a=4.3852Å and c=30.4830Å (JCPDS 15-0863). No other diffraction peaks were detected such as Bi or Te crystalline phases. The nanoparticles have sheet shapes with a size distribution of less than 200nm in
the TEM bright-field image. The inset is the corresponding selected area electron diffraction (SAED) patterns of bismuth telluride. The SAED patterns (both indexing and intensity of patterns) are in agreement with XRD results. The patterns do not show an additional diffraction spot and ring for any other phase (Figure 3(b)). The element analysis of bismuth telluride was measured by Energy Dispersive Spectroscopy (EDS) analysis of FETEM (Figure 3(c)). The atomic ratio of Bi and Te are analyzed to be 39 and 61%, respectively. This reveals that the bismuth telluride nanocrystals are composed of the stoichiometric Bi$_2$Te$_3$ phase.

**Figure 3.** (a) XRD of the solvothermally synthesized Bi$_2$Te$_3$ powders, (b) TEM micrographs and selective-area electron diffraction (SAED) as-prepared bismuth telluride nanoparticles, and (c) point STEM-EDS data of Bi$_2$Te$_3$ powders on Cu TEM grid.

The domain boundaries of the Bi$_2$Te$_3$ nanocrystals are morphologically discontinuous and scatter phonon transmission at their boundaries, regardless of the MFP of phonons. Bismuth telluride prepared with different processes results in a different phonon MFP. As emphasized earlier, one of the key issues to developing high FoM TE materials is to introduce metallic nanoparticles which are larger than phonon MFP into bulk TE materials. The phonon MFP of Bi$_2$Te$_3$ was calculated using both the Debye model and phonon dispersion model.\(^{11}\) The Debye model assumes a linear dispersion relationship between the phonon frequency and the wave vector. However, the phonon dispersion model takes into account the non-linear phonon dispersion and therefore is a more accurate estimate of the material properties. The calculated phonon MFP of Bi$_2$Te$_3$ with phonon dispersion model is about 17 nm at room temperature. The phonon MFP obtained from the Debye model is much smaller than that of the dispersion model.\(^{12,13}\) The size of the decorating metallic nanoparticles was larger than 17 nm, which is larger than the phonon MFP predicted by either model.
A cleavage surface of the Bi$_2$Te$_3$ grains coated with Au or Ag metallic nanoparticles was imaged using the SEM, micrographs from which are shown in Figure 4. In this image, the metallic nanoparticles exhibit a uniform distribution on the Bi$_2$Te$_3$ grain surface. In Figure 4(a), there are no aggregated Ag particles, and the sizes of Ag nanoparticles are fairly uniform within a range of 70–120 nm. In Figure 4(b), Au nanoparticles in the 20–25 nm size range with narrow size distribution are shown decorating Bi$_2$Te$_3$ grains.

![Figure 4](image)

Figure 5. (a) The Seebeck coefficient, (b) the electrical conductivity, (c) the Power Factor, (d) the thermal conductivity, and (e) the dimensionless Figure of Merit of Bi$_2$Te$_3$ samples decorated with 0.001 wt% / 0.05 wt% Au or 0.05 wt% Ag metallic nanoparticles, using Bi$_2$Te$_3$ as starting material at room temperature. (f) The dimensionless FoM of nano-composite samples (NC1, NC2) and zone-melted sample (ZM) in comparison with the data measured from Au or Ag nanoparticles decorated Bi$_2$Te$_3$ samples$^3$ (dashed line).

![Figure 5](image)
Figure 5 shows (a) Seebeck coefficient, (b) electrical conductivity, (c) Power Factor (PF), (d) thermal conductivity, (e) Figure of Merit, and (f) comparison of FoM from literature value of the samples. The Seebeck coefficient of Bi$_2$Te$_3$ with Au or Ag metallic nanoparticles decorated on its grain surface was higher than that of Bi$_2$Te$_3$ without nanoparticles (Figure 5(a)). It was thought that the energy level bending at the interfaces (bridges) between metallic nanoparticle and bulk TE materials causes low-energy electrons to be strongly scattered while allowing high-energy electrons to be unaffected. Thus, the nanoparticle/matrix interface serves as a low energy electron filter (electron energy filtering effect). At metal/semiconductor interfaces, charge transfer between the metal and the semiconductor leads to the band bending away from the interface, characterized by the electrostatic potential. The presence of this potential causes energy-dependent scattering of electrons. The high energy electrons are unaffected by the potential, but the low energy electrons can be strongly scattered. Because the Seebeck coefficient depends on the energy derivative of the relaxation time at the Fermi energy, this type of energy filtering is precisely the prescription to increase the Seebeck coefficient of TE materials. Mathematically, we can write the transport coefficients based on the Boltzmann transport equation as:

$$\sigma = \int \sigma(E)dE$$  \hspace{1cm} (1)

and $$S = \frac{1}{qT} \int \frac{\sigma(E)(E - E_F)dE}{\int \sigma(E)dE}$$  \hspace{1cm} (2)

where, $$\sigma(E) = q^2v(E)^2D(E)\left(\frac{df}{dE}\right)$$  \hspace{1cm} (3)

$\tau(E)$ is the energy-dependent relaxation time, which can be modified to take into account the quantum-mechanical transmission probability $T(E)$, $v(E)$ is electron velocity, $D(E)$ is the density of state, and $f(E)$ is the Fermi-Dirac distribution function.

The results show that the samples of Bi$_2$Te$_3$ grains covered with 0.05 wt% Au and 0.05wt% Ag metallic nanoparticles have lower thermal conductivity than the original Bi$_2$Te$_3$ (Figure 5(d)). Despite the decrease in the thermal conductivity, the electrical conductivity doubled with the 0.05 wt% Au and Ag (Figure 5(b)). As the amount of Au and Ag increased, the Power Factor increased as well (Figure 5(c)), along with the FoM (Figure 5(e)). Compared to the values from literature, the Bi$_2$Te$_3$ decorated with 0.05 wt% Au (blue triangle) and Ag (red triangle) particles demonstrated higher FoM than that of the nano-composite (NC) samples and zone-melted (ZM) sample (Figure 5(f)). The FoM of Au and Ag decorated Bi$_2$Te$_3$ samples are above unity, which is not only significantly higher than that of the NC or ZM samples but also higher than that of state-of-art Bi$_2$Te$_3$ alloys. In general, the thermal conductivity and the electrical conductivity have a linear relationship, as indicated with the Wiedemann-Frantz law. Usually, it is difficult to improve both properties simultaneously. However, using nanoparticles we have developed a new material design to improve TE properties, using Au or Ag nanoparticle bridges that connect Bi$_2$Te$_3$ grains. This allows electron transport for maintaining good electrical conductivity, phonon scattering at the interfacing sides of the metallic nanoparticles joining one grain to another of Bi$_2$Te$_3$ reduces thermal conductivity.

### IV. Conclusion

Bismuth telluride is one of the promising materials for room temperature thermoelectric applications. In this study, solvothermal synthesis successfully produced low-dimensional nanocrystals of bismuth telluride. Bi$_2$Te$_3$ grains covered by Au or Ag metallic nanoparticles demonstrated both a higher Power Factor and Figure of Merit than pure Bi$_2$Te$_3$. The nanoparticle/matrix interface on grain geometry serves as a thermal energy retarder for phonons while allowing electrons to move across the interfaces effectively. The advanced TE material that was developed shows material properties with low thermal conductivity, high electrical conductivity, and high Seebeck coefficient which are very favorable for TE applications.

### Acknowledgments

This research was supported by the collaborative agreement between NASA Langley Research Center and Federal Highway Administration, Department of Transportation under the inter-agency agreement #IAI-1098.
References