Enhanced Thermoelectric Properties of Solution Grown $\text{Bi}_2\text{Te}_3{-x}\text{Se}_x$ Nanoplatelet Composites

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ABSTRACT: We report on the enhanced thermoelectric properties of selenium (Se) doped bismuth telluride ($\text{Bi}_2\text{Te}_3{-x}\text{Se}_x$) nanoplatelet (NP) composites synthesized by the polyl method. Variation of the Se composition within NPs is demonstrated by X-ray diffraction and Raman spectroscopy. While the calculated lattice parameters closely follow the Vegard’s law, a discontinuity in the shifting of the high frequency ($E_2^+$ and $A_{1g}^2$) phonon modes illustrates a two mode behavior for $\text{Bi}_2\text{Te}_3{-x}\text{Se}_x$ NPs. The electrical resistivity ($\rho$) of spark plasma sintered pellet composites shows metallic conduction for pure $\text{Bi}_2\text{Te}_3$ NP composites and semiconducting behavior for intermediate Se compositions. The thermal conductivity ($\kappa$) for all NP composites is much smaller than the bulk values and is dominated by microstructural grain boundary scattering. With temperature dependent electrical and thermal transport measurements, we show that both the thermoelectric power $S$ ($-259 \mu V/K$) and the figure of merit ZT (0.54) are enhanced by nearly a factor of 4 for SPS pellets of $\text{Bi}_2\text{Te}_3{-x}\text{Se}_0.3$ in comparison to $\text{Bi}_2\text{Te}_3$ NP composites. Tentatively, such an enhancement of the thermoelectric performance in nanoplatelet composites is attributed to the energy filtering of low energy electrons by abundant grain boundaries.

KEYWORDS: Thermoelectric figure of merit, nanocomposites, $\text{Bi}_2\text{Te}_3{-x}\text{Se}_x$ nanoplatelets, energy filtering, polyl synthesis

Research in the field of thermoelectricity is full of fantastic ideas,1 the materials having an electron-crystal-phonon-glass2 such as rattling semiconductors,3 alloys,4 heterostructures,5,6 and nanocomposites9–11 are proven to be efficient thermoelectrics. The efficiency is defined by the thermoelectric figure of merit $ZT = S^2\sigma T/(\kappa_e + \kappa_l)$, where $S$ is the thermoelectric power, $\sigma$ is the electrical conductivity, $\kappa$ is the thermal conductivity ($\kappa_e$ is the electronic and $\kappa_l$ is the lattice contributions) and $T$ is average absolute temperature. An ideal thermoelectric material in principle should be electrically short-circuited and thermally open-circuited with a high thermoelectric power. However, the interdependency of the three physical parameters ($S$, $\sigma$, and $\kappa$) imposes a limitation on the efficiency of thermoelectric materials, and hence a decoupling of these parameters is required to improve the figure of merit close to 2 at room temperature.1,12,13 The improvement of $ZT$ above 1 has remained a challenging task until theoretical prediction by Dresselhaus on the utilization of quantum confinement effects in nanomaterials14 followed by experimental demonstration by Venkatasubramanian on thin films12 and recent work by the Ren and Chen group on ball-milled and hot-pressed nanocomposites.5,15 Currently, the research is mostly driven in two direction: (i) to improve the quality of the materials16,17 and synthesis methods18,19 and (ii) to develop a module or device.1,13,20,21

Nanocomposites of chalcogenides (Te and Se) and pnictogen (Bi and Sb) materials have been preferably studied for their high-performance TE properties.9,22–24 While the six valley degeneracy and the narrow energy gap of $\text{Bi}_2\text{Te}_3$ (and the family of similar compounds) is attractive for good electrical conduction, its layered crystal structure leads to a poor thermal conductivity, making these layered materials most suitable for thermoelectric applications.5,25 Experimentally, it turns out that the binary $\text{Bi}_2\text{Te}_3$–$\text{Sb}_2\text{Te}_3$ and $\text{Bi}_2\text{Te}_3$–$\text{Se}_x$ compounds are the best p-type and n-type materials, respectively, for thermoelectric refrigeration.1,2,6,15 There are also various arguments

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proposed to get better performance of these compounds like the inclusion of Sb (at Bi sites) and Se (at Te sites) creates acceptor and donor levels, respectively, in the bulk band gap of Bi₂Te₃ and in turn increases the electronic conduction (and thus the power factor S²ρ). Similarly, for some other cubic PbTe₁−ₓSeₓ composites, it has been demonstrated that Se doping leads to a convergence of the degenerate electronic bands for enhanced thermoelectric performance. Furthermore, interface scattering in nanostructures filters the low energy electrons and contributes to enhanced the thermoelectric properties with a reduction in κ other than by alloying. In the specific case of Bi₂Te₃−ₓSeₓ due to the isomorphic crystal structure of Bi₂Te₃ and Bi₂Se₃, the solubility of Se in Bi₂Te₃ results in a modification of the crystalline structure and electronic density of states (DOS), which is beneficial for inhibiting the onset of intrinsic conduction and is an important factor for the thermoelectric properties of Bi₂Te₃ alloys. Additionally, the anisotropy of the layered crystal structure plays an important role, as reported for solid solutions of Bi₂Te₃ and Bi₂Se₃ and also for nanograins of Bi₂Te₃−ₓSeₓ aligned by the repressing of compacted pellets. The materials preparation method is another strategy for enhancing the performances of thermoelectric materials as different synthesis methods show different physical properties; however a deep understanding of these systems is still lacking. This provides a platform to further study the properties of doped nanocomposites within and beyond the alloy limit where modified phonon and electron transport properties are expected.

Recently, we reported on thickness dependent Raman shifts in chemically synthesized atomically thin topological insulating Bi₂Se₃ NPs. In the present report, we demonstrate temperature dependent electrical and thermoelastic transport studies on SPS pellets of chemically synthesized NP of Bi₂Te₃−ₓSeₓ. The observed results are compared with NP composites of Bi₂Te₃ and Bi₂Se₃. The study reveals enhancement in the thermoelectric power and power factor of NPs with Se doping, while the thermal conductivity remains smaller than the bulk values. Thermoelectric figure of merit is found to be ZT ∼ 0.54 for Bi₂Te₃−ₓSeₓ at 300 K, which shows the potential applicability of SPS composites of n-type NPs grown by a chemical method.

NPs of Bi₂Te₃ and Se doped Bi₂Te₃−ₓSeₓ were synthesized using a diethylene glycol (DEG) mediated polyol method. In a typical synthesis, a stoichiometric ratio of bismuth nitrate (Bi(NO₃)₃·5H₂O), potassium telluride (K₂TeO₃·H₂O), and sodium selenide (Na₂SeO₃) were dissolved in DEG with vigorous stirring followed by refluxing the mixture solution at 240 °C. Here the solvent DEG also works as a reducing agent for the elemental species. The reaction was stopped after nearly 4–5 h and the mixture was allowed to cool down to room temperature. The precipitated powder was recovered after centrifuging and washing several times using isopropyl alcohol followed by acetone. The intermediate sonication helps to remove any unreacted chemicals as well as to clean solvent residue from the surface of NPs. The synthesized powder was then dried at 70 °C for 1 h. It has been demonstrated earlier that the polyol method adopted here can produce high quality atomically thin NPs with a high yield 80–85% of final product. The as-grown and washed powder was dispersed in an isopropyl alcohol solution and was then drop casted onto silicon substrates for characterization by scanning electron microscopy (FESEM, JEOL 7001F) and Raman spectroscopy.

Raman spectroscopy measurements were conducted on a micro-Raman spectrometer (Horiba-JY T64000) in a back-scattering configuration with an excitation wavelength of 532 nm. The backscattered signal was collected through a 100X objective and dispersed by a 1800 g/mm grating under a triple subtractive mode with a spectral resolution of ∼1 cm⁻¹ and the lowest frequency of 5 cm⁻¹. X-ray diffraction measurements on synthesized powder and SPS pellets were performed using a Bruker D8 advanced diffractometer with Cu Kα radiation in the locked coupled geometry of the X-ray gun and detector.

The dried powder was compacted into macroscopic composite pellets using spark plasma sintering (SPS) in a graphite die, by applying a pressure of 40 MPa at 250 °C and a vacuum of 0.1 mbar after purging the chamber with nitrogen to avoid oxidation during pelletization. In SPS, the high current through the powder produces sparks within the grain boundaries and thus connects NPs to one another due to local heating at weak links, without much affecting the morphologies of the NPs. To avoid grain growth, the temperature for the SPS was kept just above the growth temperature (240 °C) during synthesis. Pellets of composites are shiny gray in color with a mass density more than 87% of the bulk density (7.857 g/cm³). A 10 mm long bar of width 2 mm was cut from a nearly 0.3–0.5 mm thick circular disk and used for further transport measurements using a Quantum Design PPMS instrument. A standard four probe method was used for in-plane electrical resistivity measurements followed by heating the sample from one side for thermopower and thermal conductivity measurements. For the out-of-plane thermopower measurement, a small piece of the sample is sandwiched between two gold discs; the voltage is measured while maintaining temperature gradient across the two discs. In this out-of-plane configuration, the accuracy for electrical and thermal conductivity measurements is sacrificed as current and voltage leads are shared at cold and hot ends of the sample, like two probe measurements. In a continuous-mode measurement with a 0.5 K/minute ramping rate and a 200 s step pulse for the heater leading to more than 20 min for each data point. The measurements have been performed under a vacuum of 10⁻⁵ mbar to avoid any other losses. The emissivity value of 0.3 is used for radiations loss corrections as described in the instrument manual for rough conducting surfaces.

The as-grown samples were mostly nanoplatelets having lateral dimensions of more than 2–3 μm and a thickness of a few tens of nm (Figure 1a–c). It was noted that the scaling-up...
of the synthesis results in NPs with slightly higher thicknesses than in our previous report.\textsuperscript{33} Comparatively a perfect hexagonal morphology for Bi\textsubscript{2}Se\textsubscript{3} and a truncated-edge hexagonal morphology for Bi\textsubscript{2}Te\textsubscript{3} or Bi\textsubscript{2}Te\textsubscript{2.5}Se\textsubscript{0.5} NPs were observed from the SEM images (Figure 1a–c). This might be because of the slower reactivity of the Se ions, which allows the reaction to progress slowly and thus the inherent anisotropic layered crystal structure of Bi\textsubscript{2}Se\textsubscript{3} is maintained. On the other hand, a relatively faster reactivity and a lower reduction potential of the Te ions leads to thicker NPs of Bi\textsubscript{2}Te\textsubscript{3}. The SEM images of the top (Figure 1d) and cross section (Figure 1e) views of a sintered pellet are also shown for comparison. From the significant alignment of the NPs, it might be expected that the orientation of the NPs would affect the physical properties of the resulting nanocomposites. This will be discussed later in further sections. Figure 1f shows a photograph of the compressed pellet and the rectangular bar used for the measurements. The Se composition of the NP has been estimated using EDS measurements from an average of three different sites of the SPS pellets (Figure S1 and Table 1, Supporting Information), and consequently the compositions are assigned to the various samples.

The phase purity and crystal structure of NP SPS pellets have been identified by X-ray diffraction and the spectra are shown in Figure 2a. Compared with the JCPDS data card no. 89-2009 for Bi\textsubscript{2}Te\textsubscript{3} and no. 89-2008 for Bi\textsubscript{2}Se\textsubscript{3}, these compounds have been found to exhibit rhombohedral crystal geometry (Space group R\textoverline{3}m) with no detectable impurities of other phases. The lattice parameters calculated from the peak positions of the 006, 110, and 015 planes are found to be in close agreement with the reported values (Table 2 in Supporting Information).\textsuperscript{15,34} A systematic shift of the most intense XRD peak for the 015 plane has been observed (Figure 2b). The linear contraction of the Bi\textsubscript{2}Te\textsubscript{3} unit cell volume with increased Se concentration closely follows the Vegard’s law (Figure S2 in Supporting Information).\textsuperscript{34} Broadening and shifting of the XRD peaks for the Bi\textsubscript{2}Te\textsubscript{2.5}Se\textsubscript{0.5}, Bi\textsubscript{2}Te\textsubscript{2}Se\textsubscript{0.8}, and Bi\textsubscript{2}Te\textsubscript{2}Se\textsubscript{1.8} composites suggests that Se doping introduces disorder into the crystal structures. It is noteworthy here to mention about the prominence of the XRD peak for the 006 and 0015 planes, which indicates a significant orientation of the NPs along the (001) direction. Shown in Figure 2c is the comparison of the XRD spectra of the synthesized powder and a SPS pellet of Bi\textsubscript{2}Te\textsubscript{3}. The two spectra show that crystalline NPs are significantly oriented in the 001 direction with a diminishing of 110 directions (peak at 2\theta value of 41.14\degree) in the case of the pellet after the pelletization. This is advantageous for employing the anisotropy of the crystal structure for transport measurements without tedious efforts of repressing/aligning of the NPs.\textsuperscript{35}

Recently, Raman spectroscopy has been used extensively to study the vibrational properties and electron–phonon coupling in layered Bi\textsubscript{2}Se\textsubscript{3} and Bi\textsubscript{2}Te\textsubscript{3}.\textsuperscript{33} We performed Raman spectroscopy measurements here to investigate how the compositional variations due to Se doping affect the lattice vibrations and the electron phonon interactions in NPs. The unit cell of Bi\textsubscript{2}Te\textsubscript{3} and similar compounds have three quintuple layers stacked by van der Waal’s forces and this stacking facilitates an easy cleavage along the c axis.\textsuperscript{34} A quintuple layer is an alternate arrangements of five atomic layers, Te(1)–Bi–Te(2)–Bi–Te(1), in which Te atoms exhibit two different chemical environments (assigned as Te(1) and Te(2); Figure 3b).

Figure 3. (a) Raman spectra of pure and doped Bi\textsubscript{2}Te\textsubscript{2.5}Se\textsubscript{0.5} NPs, (b) schematic diagrams for the four Raman-active normal modes, and (c) phonon frequencies versus Se composition. Raman spectra on individual NPs were recorded in the range of 20–600 cm\textsuperscript{-1}; however, for clarity, Raman shifts are shown for 20–250 cm\textsuperscript{-1}.

While chemical bonding between Bi–Te(2) in is of a pure covalent nature, it is slightly ionic but still covalent in nature between Bi–Te(1).\textsuperscript{34,35} For the Bi\textsubscript{2}Te\textsubscript{2}Se\textsubscript{1.8} compounds, it is understood that Se atoms, being more electronegative than Te, preferentially replaces Te at Te(2) sites first, followed by
random replacements of Te at Te(1) sites.\textsuperscript{34,35} Hence, it is expected that the Se doping will change the crystalline structures and lattice dynamics in a systematic manner.

With 5 atoms in the primitive cell, there are 15 dynamical modes, at the center of Brillouin zone among which 12 are the optical modes and other 3 are the acoustic modes. The observed peaks in the Raman spectra for Bi$_2$Te$_3$ (Figure 3a) are assigned to the vibrational modes $E_g^1$ (\(\sim 36\) cm$^{-1}$), $A_{1g}^1$ (62–72 cm$^{-1}$), $E_g^2$ (102–162 cm$^{-1}$), and $A_{1g}^2$ (137–172 cm$^{-1}$), respectively. Schematic diagram in Figure 3b depicts the four Raman active vibrational modes $A_{1g}^1$, $A_{1g}^2$, and the doubly degenerate $E_g^1$ and $E_g^2$ with the corresponding atomic displacements. More details of the analysis can be found in the literature.\textsuperscript{33,36} The observed Raman shifts of the various vibrational modes with Se($x$) are summarized in Figure 3c. Here, low frequency modes $E_g^1$ and $A_{1g}^1$ have very small shifts with Se doping since these modes arise due to in-phase vibrations of Bi–Te/Se(1). From the schematic in Figure 3b, it is clear that the central Te(2) atoms are the center of mass of the Raman active vibrations. Consequently, for small doping of Se atoms, which preferentially replaces Te(2) atoms, only a slight shifting in the Raman modes is anticipated for Bi$_2$Te$_{2.9}$Se$_{0.1}$, Bi$_2$Te$_{2.7}$Se$_{0.3}$, and Bi$_2$Te$_{2.5}$Se$_{0.5}$. For higher Se content NPs, the Se atoms continue to replace Te(1) atoms randomly. In our experiments a discontinuity in the Raman Shift with a splitting of the $A_{1g}^2$ and $E_g^2$ vibrational modes is observed. It is important to note that Bi–Te(1)/Se(1) atoms move out of phase in the $A_{1g}^2$ and $E_g^2$ vibrational modes, which explains the discontinuity.\textsuperscript{36} Moreover, the different ionic sizes for Te and Se atoms also account for this behavior for Bi$_2$Te$_{2.9}$Se$_{0.1}$ and Bi$_2$Te$_{2.7}$Se$_{0.3}$. The possibility of oxidation and changes in structure due to SPS in pellets has been discussed in the Supporting Information Figure S3.

Having obtained a convincing characterization of the various compositions, we performed temperature-dependent transport measurements on rectangular bars of SPS pellets (shown in Figure 1f). The electrical resistivity of the nanocomposites (Figure 4a) shows a metallic behavior and increases for a critical Se doping. From the data, it is observed that scattering of the charge carriers is temperature and doping dependent. For instance, $\rho$ increases as the temperatures decrease for Bi$_2$Te$_{2.2}$Se$_{0.8}$ nanocomposites. Moreover, for intermediate concentrations such as $x \sim 0.16, 0.3, 0.8$, and 1.8, $\rho$ increases as the temperature drops below 30 K, possibly due to the trapping of charge carriers in NPs or the scattering of electrons with a large number of interfaces or grain boundaries. The disorder in the nanocomposites is also documented by XRD and Raman analysis. Considering the narrow band gap for pure Bi$_2$Te$_3$ (0.15 eV), where donor and acceptor levels lie extremely close to the conduction and valence band edges, a small amount of Se impurity would lead to a broadening of the impurity levels.\textsuperscript{24} The Se atom substitution in Te(2) sites, being more electronegative, will increase the ionic component of the bonding between the Bi and Se atoms at these sites. The bonding then weakens in the structure and determines the energy gap of the materials.\textsuperscript{24} Thus for Bi$_2$Te$_{2.9}$Se$_{0.1}$ nanocomposites, the bond strength and hence the energy gap will increase with increasing Se, until $x$ reaches 1 (for Bi$_2$Te$_2$Se$_1$), at which composition all the Te(2) sites are occupied by Se.\textsuperscript{24,25,37} As the Se impurities increase further, the trend is expected to be reversed and the energy gap will tend to decrease with an increasing concentrations of Se atoms (when $x > 1$). Since now Se atoms will go into Te(1) sites and they tend to attract charge along the Bi–Te(1) site bonds, therefore the bismuth atoms become more electronegative, which in turn causes charge to move toward the bismuth along the Bi–Te(2) site bonds. Thus, semiconducting behavior is observed in Bi$_2$Te$_{2.5}$Se$_{0.5}$ and the rise in resistivity below 30 K (in Figure 4a) is in line with the earlier reports on solid solutions and alloys of Bi$_2$Te$_3$ and Bi$_2$Se$_3$.\textsuperscript{32,37,38} The magnitude of $\rho$ for NP composites showing higher values relative to the earlier reports

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Temperature dependence of the (a) electrical resistivity, (b) thermoelectric power, (c) lattice ($\kappa_l$) and electronic ($\kappa_e$) thermal conductivities (estimated from the Wiedemann–Franz law; see text for details), (d) thermoelectric figure of merit of Bi$_2$Te$_{2.9}$Se$_{0.1}$ NP composites. All the figures share the same color notations as shown in (d).
on ball milled and hot pressed nanocomposites\textsuperscript{9,15} leads to the comparatively poor performance of the thermoelectric figure of merit of the present solution grown NP composites. However, in the present nanocomposites, the thickness of the NP is very much smaller in comparison to the micrometer size nanocrystals in earlier reports\textsuperscript{3,15,16}. As mentioned earlier, the present SPS nanocomposites have a mass density of \textasciitilde87\%, which means that there exists a large number of grain boundaries in the nanocomposites. Here the grain boundaries also introduce trap-states, which immobilize the charge carriers and thus reduce the carrier mobility resulting into a higher electrical resistivity.

The thermoelectric power, $S$, for all NP composites have negative values down to $T \sim 5$ K (Figure 4b), showing a typical n-type behavior. The linear temperature dependence shows that the dominant transport mechanism is diffusive transport under the applied thermal gradients\textsuperscript{26}. The magnitude of $S$ for pure Bi\textsubscript{2}Te\textsubscript{3} and Bi\textsubscript{2}Se\textsubscript{3} compounds (\textasciitilde85 and \textasciitilde80 $\mu$V/K, respectively), is smaller than that of for Bi\textsubscript{2}Te\textsubscript{3}$_{1-x}$Se\textsubscript{x} composites, which is lined up with the good conductivity for the pure compounds. It is known that $S$ is very sensitive to the asymmetry of the electronic density of states (DOS) at the Fermi level ($E_F$), and a small change in the DOS is reflected in the magnitude of $S$, which in turn is related to the charge carrier density ($n$). From the linear temperature dependence of $S$, $n$ can be calculated using the semiclassical Mott-Jones formula\textsuperscript{39,40}

$$\frac{S}{T} = -\frac{\pi^2 k_B^2}{3m^*} \partial \ln \sigma(E) \bigg|_{E_F} = -\frac{\pi^2 \hbar^2 m^*}{(3\pi^2)^{2/3} k_B^2 T \ln (n^{2/3})}$$

(1)

where $k_B$ is the Boltzmann constant, $e$ is electronic charge, $n$ is carrier density, $\sigma(E)$ is conductivity, $m^*$ is the effective mass of electrons, $T$ is temperature, $E_F$ is the Fermi energy, and $\hbar$ is the Planck constant. Assuming a simple parabolic band structure and a constant $m^*$, the slope of the linear fit to $S/T$ is used to extract the carrier density in the semiconductors\textsuperscript{25,26}. Here an effective mass of $m^* = 0.36 m_e$ ($m_e$ is the electron rest mass)$^{25}$ is used for the calculations and the estimated carrier density is found to be the order of $10^{19}$ cm$^{-3}$, which lies in the range of maximum ZT values for the high-performance thermoelectric materials\textsuperscript{26}. It is noteworthy here that $n$ decreases with Se doping thereby attaining a minimum value of $9.6 \times 10^{20}$ cm$^{-3}$ for Bi\textsubscript{2}Te\textsubscript{2.7}Se\textsubscript{0.3} and $n$ increases further with increase in Se concentration for the Bi\textsubscript{2}Te\textsubscript{2.2}Se\textsubscript{0.8} and Bi\textsubscript{2}Te\textsubscript{1.2}Se\textsubscript{1.8} compositions. We also quantify the carrier concentration of Bi\textsubscript{2}Te\textsubscript{2}Se\textsubscript{0.3} pellet using Hall measurement, which yielded $n \sim 7.8 \times 10^{20}$ cm$^{-3}$, in good agreement with the estimation based on Mott-Jones formula. Enhancement in the thermopower for NP composites can be attributed to the tuning of $n$ and to the modification of the DOS due to Se doping in NPs. Interfaces and grain boundaries also play an additional role by introducing barriers for filtering low energy charge carriers$^{11,27}$ This charge carrier filtering is more prominent for Bi\textsubscript{2}Te\textsubscript{3}$_{1-x}$Se\textsubscript{x} NP composites than for pure phases. As discussed earlier, interface scattering increases the resistivity of the NPs, and this in turn here enhances the thermopower of the present NP composites. Energy-filtered enhancement of the thermopower has been reported for heterostructured superlattices where interfaces become important$^{27,28,41}$.

One of the main advantages of utilizing nanomaterials for thermoelectric applications is the reduced thermal conductivity, $\kappa$.\textsuperscript{6,23,42,43} It has been very difficult to reduce the thermal conductivity of crystalline solids below that of an alloy without creating defects, dislocations, and voids. However, it is believed that the alloy limit can be beaten by nanostructuring\textsuperscript{5,15}. The magnitude of $\kappa$ is significantly lower than that for bulk values (1 W/m/K)\textsuperscript{9} in the temperature range of $5$–$300$ K and is approaching close to the $\kappa_{\text{limit}}$ proposed by Cahill,\textsuperscript{44} which is 0.28 for superlattices of Bi\textsubscript{2}Te\textsubscript{3}.\textsuperscript{12} For all NP composites, $\kappa$ decreases with temperature and shows a small hump-like feature at typical intermediate temperatures where the electron–phonon interactions are dominant (Figure 4d).\textsuperscript{25}

The electronic contribution to the total thermal conductivity is related to the electrical conductivity and is calculated from the Wiedemann–Franz Law: $L_e = \sigma T / \kappa_e = L_e T$, where $L$ is the Lorenz factor, $2.45 \times 10^{-8}$ W/S/K$^2$.\textsuperscript{25} The possibility of heat transfer by bipolar charge carriers is ruled out from the negative sign of $S$, which means that the majority charge carriers are electrons in the present nanocomposites. The electronic $\kappa_e$ and lattice ($\kappa_l = \kappa - \kappa_e$) contributions are separately presented in the Figure 4c. It is clearly seen here that $\kappa_l$ dominates over $\kappa_e$ for the whole temperature range, illustrating the importance of the microstructural aspects of NP composites. From the temperature-dependent transport studies, even though $\rho$ is comparatively on a higher scale, the increase in $S$ is significant, thus increasing the power factor ($S^2/\rho$). Furthermore, both the increased power factor and the reduced $\kappa$ result in an enhanced figure of merit in the present NP composites (Figure 4d).

Now, we discuss the effect of Se doping on the physical properties of nanocomposites at room temperatures. As shown in Figure 5, the $\rho$ increases with Se concentration and finds a maximum value for Bi\textsubscript{2}Te\textsubscript{2}Se\textsubscript{2.8}. The thermopower values change drastically from $-85$ $\mu$V/K for Bi\textsubscript{2}Te\textsubscript{3} to $-259$ $\mu$V/K for Bi\textsubscript{2}Te\textsubscript{2}Se\textsubscript{0.3} NPs, indicating an enhancement of almost 3 times. Both the physical parameters ($\sigma$ and $S$) are mostly affected by the $n$, which is the number of charge carriers (DOS at $E_F$). Thus, Se doping in the NP composites tunes the $n$ in the regime of $10^{19}$–$10^{20}$ cm$^{-3}$, which is supposed to be advantageous for thermoelectric applications.\textsuperscript{2,6} The magnitude of $\kappa$ is reduced with Se doping for Bi\textsubscript{2}Te\textsubscript{2}Se\textsubscript{0.3} and further increases attaining a maximum value for Bi\textsubscript{2}Te\textsubscript{1.8}Se\textsubscript{1.2}, which is in close agreement with the reports on alloys and solid solutions.\textsuperscript{29,46} With all these parameters, the room temperature thermoelectric figure of merit
Antisite defects play an important role for chalcogenide thermoelectric materials. This has been reported for Bi₂Te₃ thin films where the most stoichiometric sample has high crystallinity, high thermopower, and high electron mobility.[47,48] However, the c-axis lattice constant, thermopower, and electron mobility decrease with excess Te, and the crystallinity clearly degrades. All of these observations have been explained as arising from antisite defects in which excess Te occupies the Bi lattice sites and behaves as an n-type dopant and the antisite defects will dominate over vacancies. Cho et al. concluded that both the reduced lattice constants and the reduced thermopowers are attributed to heavy n doping via antisite defects. This is not the case in the present samples, as the composites are of a crystalline nature with a systematic reduction in the unit cell volume. Moreover the thermopower is higher for the doped sample than for the pure samples in contradiction to the report by Cho et al.,[47] where the thermopower is smaller for samples with antisite defects.

Anisotropy in bulk-layered chalcogenide structures is an important factor, as important physical parameters can be different along different directions. For single crystal solid solutions of Bi₂Te₂.₇Se₀.₃, the electrical conductivity (1/ρ) is four times higher along the ab-planes, due to the same type of atoms in the basal planes, than along the c axis; κ is two times smaller along the c axis due to possible damage in the cleavage planes.[52] Yan et al.[15] also demonstrated that repelleting orients the nanograins in a typical crystal direction and thus improves the ZT by 22%. However, it was reported that S remains isotropic and the improvement in ZT is due to anisotropic conductivities.[15] In our measurements, we have observed that S is anisotropic when measured with the temperature gradient across the two faces (Figure 6 top right inset) of the pellet. The room temperature S(a) value is much lower than the S(b) values with the temperature gradient along the lateral side (Figure 6, bottom left inset) of the SPS pellet. This anisotropic S can be understood by modeling the connectivity of the NPs and the density of the grain boundaries in the two directions. It is shown in Figure 2c that the SPS pelletization significantly aligns the NPs (XRD comparison of the powder and SPS pellet). The alignment of these two-dimensional NPs during SPS pelletization mounts-up NPs along the top-bottom surfaces, where a comparatively large surface area finds a relatively good connectivity with only a small amount of grain boundaries. This would lead to a lower probability for filtering low energy charge carriers, and thus S has relatively smaller values (Figure 6 curve a). On the other hand, the situation is more complicated for other directions with more lateral connectivity coming from the NPs and yet more scattering coming from the large number of grain boundaries. The temperature dependence of S is linear, demonstrating that the transport is diffusive in the planar direction; however, it is nonlinear across the pellet. This demonstrates that the scattering of the charge carriers is different in the two directions. Recently, two-dimensional nanostructures of Bi₂Te₃ and Bi₂Se₃ have also been studied for their topological properties where surface states enhance their thermoelectric properties.[49,50] Further studies on the linear (in-plane) and nonlinear (out of plane) temperature dependence of S are required for these NPs.

In summary, we have demonstrated that the facile and cost-effective polyl method can be scaled up to synthesize high quality Bi₂Te₂.₇Se₀.₃ NPs, which enables the preparation of macroscopic pellets by spark plasma sintering with preferential alignment along the c axis. Highly anisotropic thermoelectric power values are found for the in-plane and out-of-plane S(T) and this anisotropy is tentatively attributed to anisotropic energy filtering in the two directions by grain boundaries. By adjusting the Se composition, the optimal thermoelectric performance is found for the Bi₂Te₂.₇Se₀.₃ NP composite, which exhibits an S value of −259 μV/K and a figure of merit ZT of 0.54 at room temperature. Further research is required to improve the electrical conductivity of the nanocomposite while still keeping the thermal conductivity low either by using different composite processing parameters or by introducing other conducting polymers with intrinsic lower thermal conductivities.

ASSOCIATED CONTENT

Supporting Information
Additional information and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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