Interface Driven Energy Filtering of Thermoelectric Power in Spark Plasma Sintered Bi$_2$Te$_{2.7}$Se$_{0.3}$ Nanoplatelet Composites

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ABSTRACT: Control of competing parameters such as thermoelectric (TE) power and electrical and thermal conductivities is essential for the high performance of thermoelectric materials. Bulk-nanocomposite materials have shown a promising improvement in the TE performance due to poor thermal conductivity and charge carrier filtering by interfaces and grain boundaries. Consequently, it has become pressingly important to understand the formation mechanisms, stability of interfaces and grain boundaries along with subsequent effects on the physical properties. We report here the effects of the thermodynamic environment during spark plasma sintering (SPS) on the TE performance of bulk-nanocomposites of chemically synthesized Bi$_2$Te$_{2.7}$Se$_{0.3}$ nanoplatelets. Four pellets of nanoplatelets powder synthesized in the same batch have been made by SPS at different temperatures of 230, 250, 280, and 350 °C. The X-ray diffraction, transmission electron microscopy, thermoelectric, and thermal transport measurements illustrate that the pellet sintered at 250 °C shows a minimum grain growth and an optimal number of interfaces for efficient TE figure of merit, $ZT \sim 0.55$. For the high temperature (350 °C) pelletized nanoplatelet composites, the concurrent rise in electrical and thermal conductivities with a deleterious decrease in thermoelectric power have been observed, which results because of the grain growth and rearrangements of the interfaces and grain boundaries. Cross section electron microscopy investigations indeed show significant grain growth. Our study highlights an optimized temperature range for the pelletization of the nanoplatelet composites for TE applications. The results provide a subtle understanding of the grain growth mechanism and the filtering of low energy electrons and phonons with thermoelectric interfaces.

KEYWORDS: Thermoelectric figure of merit, Bi$_2$Te$_{2.7}$Se$_{0.3}$ nanoplatelet composites, spark plasma sintering, interfaces, grain boundaries, energy filtering

Recently, the bulk nanocomposite approach has been shown to be advantageous over their bulk counterparts to achieve an enhancement in the high thermoelectric (TE) figure of merit, primarily due to poor thermal conductivity or quantum confinement effects although the electrical conductivity of those highly disordered nanomaterials is usually compromised.1,2 In this context, the designing and engineering of interfaces and preferential phonon scattering centers in nanocomposites have become an important field of research to improve the performance of future TE materials.3,4 The efficiency of the TE materials is scaled as a dimensionless TE figure of merit, $ZT = S^2\sigma T/(\kappa_e + \kappa_l)$, where $S$ is the Seebeck coefficient, $T$ is the absolute temperature, $\sigma$ is the electrical conductivity, and $\kappa_e$ and $\kappa_l$ are, respectively, the electronic and lattice contributions to the thermal conductivity.5 Thus a good TE material should have a high Seebeck coefficient, a high electrical conductivity, and a low thermal conductivity. Combining all three physical parameters, doped semiconductors are found to be the best TE materials.5–7 Though nanostructure composites are promising candidates for...
enhanced TE properties,9 yet the thermodynamical instability of enormous grain boundaries and interfaces limits their application range and reproducibility of performance for TE applications.6 Therefore, to optimize the processing parameters and to identify the effective range of applicability, it is significant to study how the thermodynamical environment of nanocomposite preparations affects their physical properties.

The chalcogenides are among the most studied TE materials and their application spans over the whole temperature range of 100–1000 K, with every material representing a typical temperature range.5,6,10–12 For instance, Bi2Te3 and related compounds are suitable for low-temperature refrigeration,2 while PbTe, Co,Sb12, and ZnSb based compounds are best suited for high temperature power generation.10,13,14 The temperature range of TE application is defined by the electronic band structure, crystal structures, and preparation methods, such that the decoupling of all the interdependent physical parameters (S, σ, and κ) could be possible.14–16 After a resurgence of TE research,2,15 the nanocomposites of Bi2Te3 and related compounds have shown potential improvement in ZT above 1 for room temperature TE applications with a large number of interfaces.1,17 On this note, studies on high performance bulk nanoplatelet-composites (NPCs) are of interest because of facile and scalable synthesis with anisotropic properties due to grain boundary/interface arrangements.18–22

The interfaces perform an energy-filtering effect that preferentially scatters phonons which contribute strongly to the thermal conductivity.2,12,24 In addition, the energy barriers introduced by the interfaces also block the low-energy electrons and therefore decrease the average heat transported per carrier.3,25 Thus, the introduction of interfaces exhibits significant promise to suppress thermal conductivity with minimized decreasing of electrical conductivity, leading to an improved ZT. The low energy charge carrier filtering by interfaces has been demonstrated in chalcogenide materials composed of thin film superlattices,1 nanograins,26 heterostructures,24 and nanoinclusions.27,28 From the comparison of NPCs with nanoparticles composites,2 it has been understood that nanoparticles might not be as effective as a filter as nanoplatelets in bulk nanocomposites, because the low energy electron wave functions might go around the nanoparticles.8 However, for the present case of layered NPs, the charge carriers and phonons seem to couple in a unique fashion such that interfaces can enhance the electronic and thermal transport properties, anisotropically.5,18 Additionally, for the TE nanocomposites, the microstructure, mean-particle-size, particle size distribution, materials densification, and grain-boundary properties are very important parameters. Therefore, it is important to optimize the processing conditions so that a proper choice of material with higher and more stable ZT could be produced.

Previously, we have reported on the enhanced TE properties of solution grown composites of Bi2Te3−xSe x nanoplatelet with a ZT of 0.54 for Bi2Te3−0.3Se0.3 composites.18,30 In the present report, we highlight the effects of the thermodynamical environment, during the preparation of the composites, on the physical properties of the NP composites. With the TE and thermal transport measurements, a SPS temperature of 250 °C has been optimized for comparatively stable ZT ~ 0.55, which is within the error limit in comparison to the previous report.18 The current study emphasizes the energy filtering due to a large number of anisotropic interfaces and grain boundaries in the bulk-NPCs and the effect of the SPS temperature on the typical temperature range of their applications, which has not been addressed extensively in the literature to the best of our knowledge.

Our prior work on the polyol synthesis method has produced high quality crystalline NPs of Bi2Te3, Bi2Se3, and Se doped ternary Bi2Te1−xSe x (0 ≤ x ≤ 3).18,30 We have shown that the cost-effective polyol method can be easily scaled up to a few gram quantity of the NPs in each growth. More details of the synthesis and washing of the NPs can be found in the previous literature.18,30 Four different samples, named as (i) SPS-230C, (ii) SPS-250C, (iii) SPS-280C, and (iv) SPS-350C, have been pelletized in a graphite die by applying a pressure of 40 MPa using SPS at various temperatures (i) 230 °C, (ii) 250 °C, (iii) 280 °C, and (iv) 350 °C, respectively. The SPS chamber was kept under a vacuum of 0.1 mbar after purging with nitrogen to avoid oxidation during pelletization. Disc shape pellets with a 12 mm diameter and a thickness of 0.3–0.5 mm were obtained. The mass densities of the pellets are estimated to be greater than 87% and found to increase with increasing SPS temperatures; however this is not the case for SPS-230C, where the density is roughly 83% of bulk value. It is believed that high current during SPS produces sparks within the grain boundaries of NPs and these sparks connect the weak links of NPs by local heating, without much affecting the morphologies of the samples. However, for the present NPCs, the SPS operating at higher temperatures yields grain growth and thus significant modification to the physical properties of the NPCs.

The crystalline structure of the Bi2Te2−0.3Se0.3 compounds, similar to the rhombohedral families of Bi2Te3 compounds, has a layered geometry with each unit cell consisting of three quintuple layers stacked together with van der Waals forces. A quintuple layer consists of an alternate arrangement of Bi and Te atoms such as Te(1)−Bi−Te(2)−Bi−Te(1), where Te atoms are distinguished with two different chemical environments.31 As reported earlier, Se has complete solubility in Bi2Te3 with a preferential occupancy at two different Te sites, with increasing Se concentrations.18 In the case of Bi2Te2−0.3Se0.3 NPs, comparatively more electronegative Se atoms occupy Te(2) sites relative to Bi2Te3 nanocomposites.18,31 The X-ray diffraction (XRD) patterns of the SPS pellets are shown in Figure 1 (Bruker D8 diffractometer, with a Cu Kα radiation in the locked-coupled geometry of the X-ray gun and detector). From the comparison of the XRD spectra with the JCPDS data card no. 50-0954, and the observed prominence of the 006, 0010, and 0015 peaks, it is understood that NPs have a preferential orientation in the c-direction. In other words, these NPs tend to align themselves together during pelletization.18

![Figure 1](dx.doi.org/10.1021/nl302017w/1NanoLett.2012,12,4305-4310)
The lattice parameters estimated from the XRD peaks are found to be $a = 0.437$ nm and $c = 2.98$ nm for SPS-250C, within the error limit for other NPCs. The comparatively sharper XRD peaks for SPS-280 and SPS-350 samples illustrate the grain growth at these higher temperatures. It is interesting to note that the 104 peak is appearing gradually for pellets except for sample SPS-230C. For the SPS-350C sample, the peak corresponding to 104 planes is dominating over the other diffraction peaks, which suggests the reorientation of grains after crystallization of the interfaces; however, the exact reason for such a grain reorientation is not clear at this stage. To understand this effect further, we carried out cross section TEM measurements, which will be discussed in the later sections of this paper.

The morphologies of the NPCs have been carefully examined by field-emission scanning electron microscopy (FESEM, JEOL 7001F). Figure 2 displays representative SEM images of the cross-section view of the pellets of SPS-230C and SPS-350C (Figure 2a and b). The estimated thickness of the SPS-230C NPCs is less than $\sim 40$ nm (Figure 2a), and an apparent grain growth has been observed (Figure 2b) for SPS-350C with a thickness of 150 nm or higher. The top (Figure 2c) and cross section (Figure 2d) views depict the significant orientation of the SPS-350C NPCs. It was reported earlier that this typical orientation affects the physical properties of the NPCs significantly.\(^{18}\)

The temperature-dependent TE transport measurements, using a Quantum Design PPMS instrument, have been carried out on a 10 mm long bar with a width of 2 mm cut from the circular disk compacted by SPS. The four-probe method is used for electrical resistivity measurements followed by thermopower and thermal conductivity measurements by heating the sample from one side. In a continuous-mode measurement with a 0.5 K/min ramping rate and a 200 s step pulse applied to the heater, leading to more than 20 min for measuring each data point. To avoid thermal losses due to radiation and other sources, the measurements have been performed under a vacuum of $10^{-5}$ mbar. The electrical and TE transport data are shown in Figure 3. The Seebeck coefficient, $S$ (Figure 3a), has a linear dependence with temperature showing a diffusive transport for NPCs SPS at low temperatures such as SPS-230C and SPS-250C. The rough estimation of the number of charge carriers, using the classical Mott–Jones formula and Hall measurements, lies in the range of $10^{18}–10^{19}$ cm$^{-3}$.\(^{18}\) The temperature dependence of the electrical resistivity, $\rho(T)$ (Figure 3b), shows a metallic behavior with different phonon scattering mechanisms (from the slope $d\rho/dT$) in each pellet. Apparently, the contribution from structural disorder effects can be estimated qualitatively from the values of the residual resistivities, which decrease for the high temperature SPS NPCs. As expected, the $\rho(T)$ value is reduced for NPCs sintered at high temperatures. For instance, the sample SPS-230C has high $\rho$ values at all temperatures, while the samples SPS-280C ($\sim 36$ $\mu\Omega$-cm) and SPS-350C ($\sim 31$ $\mu\Omega$-cm) have a comparatively better electrical transport in comparison to earlier reports.\(^{18,29}\) This improvement in the electrical conduction for the NPCs is arising from the grain growth or rearrangements of the grain boundaries during SPS at high temperatures. The $\rho$ and $\kappa$ are inter-related through the Wiedemann–Franz law\(^{13,15}\) and have the similar trends as one another for each SPS sample. The contribution from the lattice thermal conductivity is also apparent due to the grain growth in the NPCs. The higher-$\rho$ and smaller-$\kappa$ values for SPS-230C result from the poor connectivity of the NPCs to each other and the low mass density of the NPCs.\(^{2,13,25}\) The $\kappa$ values (in Figure 3c) are increasing systematically with the SPS temperatures and approaching close to the bulk values measured at 300 K of 1.2 W/m·K$^2$ for SPS-350C.$^{13,15}$

The power factor has the highest value for SPS-250C and then decreases in the sequence of SPS 280C followed by SPS 230C and SPS 350C samples. Even though the high
temperature SPS is leading to a better electronic conduction, yet the power factor $S^2/\rho$ (inset in Figure 3d) does not improve with respect to the SPS-250C. The significant reduction of $S$, for SPS-280C and SPS-350C, appears to be the obvious reason for the deprived power factor with the SPS temperatures. The power factor for SPS-230C and SPS-350C NPCs is found to be nearly equivalent but certainly has different reasons, while the high $\rho$ values of SPS-230C is responsible for the poor performance and the low $S$ and high $\kappa$ values for SPS-350C. This signifies the need for the present study of complexity in the nanostructured materials for TE applications. Comparing the room temperature values, the SPS-250C with a $ZT \sim 0.55$ has a better TE performance than other NPCs. The room temperature $ZT$ value for SPS-250C is also higher than the reported for the high temperature SPS pelletized bulk NPCs of Bi$_2$Te$_3$ NPs prepared by a solution method. The surprising poorer $ZT$ for SPS-280C and SPS-350C is because of the concomitant rise of $\sigma(1/\rho)$, $\kappa$ with reduced $S$ values, whereas very high $\rho$ values, though with high $S$ and low $\kappa$, lead to a poor $ZT$ for SPS-230C. As a consequence, the unexpected poor values of $ZT$ for SPS-280C and SPS-350C demand a further investigation on the high temperature states and microscopic details of the NPCs.

During SPS at high temperatures, the evaporation of the elemental species from the NPCs is suspected. To understand further the reason for this speculative evaporation, we have performed a thermogravimetry analysis (TGA) of two end samples, SPS-230C and SPS-350C (Figure 4a). The data illustrate a maximum mass loss of about 5% at 600 °C. For the present NPCs, our concern is the weight loss below 350 °C, which is the highest SPS temperature utilized. The results showed only <1% mass loss below 350 °C. The absence of impurity phase peaks in the XRD spectra (Figure 1) suggests that there is no significant change in the crystal structure of the NPCs with SPS. Thus less than 1% mass loss is insignificant to affect the crystal structure of the compounds and might not account for the drastic changes in transport properties.

Another speculative reason for the poor TE performance is the rearrangements of grain boundaries and interfaces which might give rise to extra entropic contributions from the NPCs. As reported earlier, the interfaces play an important role via filtering charge carriers in TE nanocomposites. To understand further the effect of high temperature SPS on physical properties and to estimate the thermal response of the NPCs, we have carried out differential scanning calorimetry (DSC) measurements in the temperature range of 100−500 °C. For DSC measurements, a small 2 × 2 mm$^2$ square piece (~30 mg) was cut from the pellets and was kept in an aluminum pan along with an identical empty one as a reference. Each sample has gone through a cycle of heating−cooling−heating at the rate of 5 °C/s, in the temperature range of 100−500 °C. An argon atmosphere was maintained inside the chamber to avoid possible oxidation during heating−cooling cycles. We cautiously avoided heating the pellets up to the melting temperature of the parent bulk Bi$_2$Te$_3$ (584 °C), as this might cause the evaporation of materials during the experiment. Given that the nanocomposites are ad-mixtures of the grains and grain boundaries, the heat flow in the NPCs is expected to be governed by the interfaces and grain boundaries. In DSC measurements, the thermodynamic instability of nanostructures is reflected as an endothermic peak due to the consumption of the heat flow in grain growth and as a heat release exothermic peak for rearrangements or crystallization of the interfaces and grain boundaries. An irreversible exothermic peak is reported for composites of copper and silver nanoparticles where the stored surface energy is released during the first heating cycle of the DSC measurements.

Shown in Figure 4b, the SPS-230C has a broad exothermic peak in the temperature range of 150−500 °C, appearing perhaps due to the crystallization of a large number of...
interfaces between the smaller thickness NPs. As mentioned earlier, the smaller thickness of the NPs in the SPS-230C sample is apparent from the broadness of the XRD peak widths of the 006, 0010, and 0015 diffraction peaks (Figure 1) and SEM images (Figure 2). With the smaller thickness of the NPs, a higher number of interface and grain boundaries can be expected in the SPS-230C sample. A very small exothermic peak at 383 °C is observed for all of the SPS samples. The peak has been attributed to the presence of Bi₂TeO₅ without concrete justification. Our XRD and small-angle electron diffraction (SAED) measurements do not support presence of oxides either. Therefore, the origin of this exothermic peak is still elusive. For SPS 230C, two endothermic peaks in first heating at 419 and 449 °C are also observed and attributed to the eutectic point of Bi–Te phase diagram and melting point of nonreacted Te, respectively. These two peaks, however, are not seen for the other NPCs, suggesting that the presence of Te is not intrinsic to the other NPCs. We would like to remind the reader here that the NPs are synthesized at the refluxing temperature of 240 °C, and thus a significant grain growth during SPS is less likely below 240 °C and is more likely for samples sintered at temperatures above 240 °C. The plateau-like thermal response up to 370 °C for SPS-250C, SPS-280C, and SPS-350C suggests that the heat flow only rearranges the interfaces during the heating process. The abrupt rise in heat flow above 430 °C for SPS-250C and SPS-280C may be related to the sudden crystallization of several NPs. In the case of the SPS-350C sample, the flat response of the heat flow with a disappearance of the exothermic peak above 400 °C suggests that there is only a small amount of involved-contribution from a very much smaller number of interfaces. The crystallization or rearrangements of the interfaces and grain boundaries is an irreversible process, so that when a sample has been treated with a heating cycle, the interfacial arrangement is expected to be locked inside the pellets. To confirm this conjecture, all of the NPCs have been given a further slow cooling and reheating cycle. After the first-heating cycle, all of the NPCs have shown a disappearance of the broad exothermic peak during first-cooling and second-heating (Figure 4c), which is a signature of an irreversible contribution from the stored surface energy or from the interface crystallization in the pellets. The pairing of exothermic peak in first cooling and endothermic peak in second heating, for all NPCs, are appearing perhaps because of the eutectic temperature of Bi–Te in Bi₂Te₃ phase diagram. A systematic variation in the crystallization peak (Figure 4c, inset i) in the thermogram has been observed with respect to the SPS temperature. The endothermic peak in the second heating (Figure 4c, inset ii) does not show variations in peak position, probably due to the irreversible arrangements of the interfaces during first heating and cooling. The crystallization during the first cooling and the melting in the second heating with the absence of a first broad exothermic peak justifies our argument of rearrangement of interfaces. The crystallization of the interfaces at a high temperature supports the transport data where both the electrical and the thermal conductivities are increasing for the high temperature SPS samples. Thus, when a sample is sintered at a particular temperature, the arrangements of the interfaces appear to be locked during the SPS at that temperature. Since there is no change in the composition, the thermal response of the pellets is arising due to the thermodynamic environment of interface structure locked inside the NPCs. These interfaces are filtering the low energy heat and charge carriers in a unique fashion and consequently affecting the physical properties of the NPCs.

Now we will discuss the microstructural aspects of the NPCs to understand the anomalous TE response of the NPCs, investigated by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) measurements (JEOL JEM 2100F) operated at an accelerating voltage of 200 kV (C₀ = 0.5 mm, Scherzer defocus = −43 nm). The TEM samples for a cross section view of the pellets were prepared by standard dimpling, followed by a final thinning and polishing by a focused ion beam (Nova Nanolab 600i, FEI). The TEM micrographs shown in Figure 5 provide an appropriate explanation and support to the argument of interface rearrangements and grain growth at high temperature SPS. The grain growth can be perceived from the comparison of the cross section TEM images for samples SPS-230C (Figure 5a) and SPS-350C (Figure 5c). As pointed out earlier, the NPs self-orient along the c-axes and are stacked one over the other inside the NPCs. The SAED index pattern, taken on the cross-section of the NPCs with the zone axis of [2110] for SPS-250C and [2110] for SPS-350C, of the rhombohedral crystal structure shows that the NPs have been grown in the c directions. The arrows in TEM images are pointing to the c axes [0001]. Thus from the TEM images, the explanation of grain growth and interface crystallization, as speculated from the TE transport and thermal response of NPCs, is reasonable. It was reported earlier that the NPCs have anisotropic TE power and the in-plane S is two times higher than the out-of-plane S. This difference is explained on the basis of the different scattering mechanism in the two directions. The TEM images in Figure 6 illustrate the weak link connectivity between the NPs in two different directions of the in-plane and out-of-plane micrographs. It is clear that the top-bottom stacking has larger area connectivity between the NPs and that the crystallization of the interfaces is straightforward. On the
Figure 6. Cross section TEM images showing weak links along the two directions: (a) top—bottom stackings and (b) head-to-head joining. Scale bars are 5 nm.

other hand, the connectivity is poorer in the case of the in-plane head-to-head stacking. In both cases, the interfaces are playing an important role by forming barrier networks for filtering the carriers of both the heat and electrical energy; however, the energy filtering from the interfaces is more effective with the in-plane transport measurements.

In conclusion, we have demonstrated the optimized plasma sintering conditions and temperature range of the pelletization for Bi$_2$Te$_2$Se$_{0.3}$ NPCs for TE applications. The NPCs are oriented along the c-axes and are highly anisotropic. The NPC sintered at 250 °C shows a ZT~0.55, with the optimal charge carrier filtering effects originated from the interfaces and grain boundaries. However, the high temperature SPS (350 °C) results in high electrical and thermal conductivities with a reduced thermopower and a poor ZT. Thermal transport measurements and thermal analysis using TGA and DSC suggest that the crystallization and rearrangements of the interfaces are playing an important role in deciding the physical properties of the Bi$_2$Te$_2$Se$_{0.3}$ NPCs. The cross section TEM imaging indeed confirms the grain growth and interface rearrangement. Our results highlight the subtle understanding of engineering interfaces and grain boundaries needed to improve the TE properties of bulk nanocomposites, particularly of those layered nanomaterial TE composites.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**