Evaluating the effect of grain size distribution on thermal conductivity of thermoelectric materials

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Abstract
The influence of grain size \((d)\) on the thermal conductivity \((k)\) of thermoelectric \((TE)\) materials has been well established through experimental studies. However, the effect of grain size distribution, described by \(S_d\), on \(k\) has not been reported before. Since thermal conductivity is a key contributor to the figure of merit \((ZT)\) for thermoelectric materials, studying the effect of grain size distribution, an important microstructural descriptor, on \(k\) is necessary. In the current study we are evaluating the effect of \(S_d\) on the \(k\) of thermoelectric materials by using data reported in literature on bismuth telluride \((\text{Bi}_2\text{Te}_3)\) and lead telluride \((\text{PbTe})\). We first check for correlations between \(k\) and \(d\). In literature, mathematical correlations between lattice thermal conductivity \((k_l)\) and \(d\) have already been reported but the same is missing for electronic thermal conductivity \((k_e)\) and \(d\). By analysing literature data for bismuth telluride and lead telluride at 300 K, we identified a linear correlation between \(k_e\) and \(d\), wherein an increase in \(d\) leads to an increase in \(k_e\). This dependence of \(k_e\) on \(d\) was combined with the dependence of \(k_l\) on \(d\) to establish the overall dependence of \(k\) on \(d\). Subsequently, the grain size distribution effect was imposed by using a log normal distribution. The analysis revealed that for a given grain size, an increase in \(S_d\) leads to lowering of the thermal conductivity of the material. The analysis was also extended to bimodal grain size distributions wherein the microstructure was designed in a way to contain a mixture of both nanocrystalline and microcrystalline grains.

1. Introduction
Thermoelectric \((TE)\) materials are gaining more importance due to their ability to convert the available enormous amount of waste heat energy into useful electrical energy. This conversion of energy is due to the Seebeck effect. Solid state power generation, and optoelectronics are some of the sectors where TE materials can be used effectively [1]. The main challenge associated with a TE material is to increase the energy conversion efficiency which is quantified by figure-of-merit \((ZT)\). The \(ZT\) can be represented as

\[
ZT = \frac{s^2 \sigma T}{k},
\]

where, \(s\), \(\sigma\), \(T\), and \(k\) are the Seebeck coefficient, the electrical conductivity, absolute temperature and thermal conductivity respectively [2]. The total thermal conductivity of a system is the algebraic sum of its electronic and lattice thermal conductivities i.e. \(k = k_e + k_l\), where \(k_e\) is electronic thermal conductivity and \(k_l\) is lattice thermal conductivity. The \(k_e\) mainly depends on the electrical conductivity and Lorentz number of the materials and it can be described as \(k_e = L \sigma T\), where \(L\) is Lorentz number = \([1.5 + \exp\left(-\frac{151}{T}\right)] \times 10^{-8} \text{W} \Omega \text{K}^{-2}\), \(s\) is experimentally measured in \(\mu \text{V} \text{K}^{-1}\), \(T\) is the absolute temperature; albeit some studies have revealed a grain size dependence of \(k_e\) [3, 4]. The \(k_l\) depends upon the lattice vibrations of the material and the creation of short-range order in the lattice to sufficiently scatter the phonons to reduce the lattice thermal conductivity. Nanostructuring methodology [5, 6] enables the introduction of different length scale microstructural features which can effectively scatter most of these three wavelength regimes of phonons i.e. short, mid and long
wavelengths to reduce the lattice thermal conductivity \((k_l)\) of the materials \([7, 8]\). There are other approaches to increase \(ZT\) such as using dopants \([9–11]\) and varying the level of doping \([12–14]\). However, decreasing the grain size is an effective way to enhance the \(ZT\) \([15–17]\), because dense grain boundary area significantly enhances the phonon scattering and thus result in lower thermal conductivity. This can be seen from the work of Rowe et al \([18]\). Their study compared the conversion efficiency (calculated from \(ZT\)) of n-type Si-Ge polycrystalline materials having grain size 10 \(\mu\)m and 0.1 \(\mu\)m respectively at 1000 K. The sample having 10 \(\mu\)m grain size and 0.1 \(\mu\)m grain size showed an improvement of 14% and 30% over the Si-Ge single crystal. The dependence of Seebeck coefficient on grain size was addressed by Gao et al \([19]\). In their study, the Boltzmann transport equation was used with the grain boundary scattering effect as the boundary condition for electron transport in grain. The validation of the proposed model was done by comparing the values of Seebeck coefficient for CoSb\(_3\) bulk samples with the values obtained from model-based calculation. The Seebeck coefficient for CoSb\(_3\) bulk samples having average grain size varying from 2 nm to 5 \(\mu\)m was calculated, showing an exponential decrease with an increase in grain size, and found to match with the experimental data \([20]\). However, tuning \(s, \sigma, \) and \(k\) independently is difficult. The Seebeck coefficient decreases with an increase in charge carrier concentration, whereas electrical conductivity and thermal conductivity increase with carrier concentration \([21]\). Increasing the charge carrier concentration to improve the electrical conductivity, \(\sigma\), leads to a concomitant increase in \(k\), the electronic thermal conductivity and thus an increase in \(k_l\). Although Synder et al \([22]\) optimized the carrier concentration to maximize \(s\sigma\) value for Bismuth Telluride \((\text{Bi}_2\text{Te}_3)\) and Pichanuskorn et al \([23]\) optimized the value of Seebeck coefficient to maximize the power factor in TE materials, the associated problem of increase in \(k\) cannot be ruled out. Hence to maximize \(ZT\), the only option is to decrease \(k\) without reducing \(\sigma\) and this can be achieved through grain size refinement, where the short-range order created by the introduction of grain boundaries effectively scatters the phonons and reduces the total thermal conductivity \([1, 22]\). Towards this end, many studies have focused on reducing \(k\) through nanostructuring of the TE material. By reducing the grain size from 30 \(\mu\)m to 10 \(\mu\)m for \(\text{Bi}_2\text{Te}_3\), the \(k\) value was decreased from 1.6 to 0.61 W mK\(^{-1}\) \([24–26]\).

Various models were employed to describe the change in \(k\) including \(k_l\) & \(k\), with grain size. Kinemuchi et al \([27]\) focused on improving the figure of merit \((ZT)\) through boundary scattering in In\(_2\)O\(_3\). They employed Debye-Callaway model to determine the phonon thermal conductivity and Wiedemann–Franz equation to evaluate the electronic thermal conductivity of samples having different average grain size ranging from 20 nm to 2 \(\mu\)m. Both the \(k_l\) and \(k\) values showed a decrease with the reduction in average grain size and increase in temperature. The calculated ZT value for 30 nm grain size sample at 300 K was reported to be 0.06 which is very close to the experimentally determined ZT for the same sample \((0.07)\). The validation of Debye-Callaway model was also done by Kinemuchi et al in a previous work on Ga doped ZnO \([28]\). The study showed a good agreement between the experimental data and the model predictions for thermal conductivity for samples having grain sizes in the micro and nano scale. Similarly, Popescu et al \([29]\) calculated the \(k_l\) of Bi doped PbTe system utilising the Holland–Callaway model and showed its agreement with the experimental data.

There are some studies where the variation of \(k\) with grain size was calculated directly instead of calculating both \(k_l\) & \(k\). Cao et al \([30]\) studied the variation in thermal conductivity of hot pressed PbTe bulk samples having grain sizes varying from 200 to 400 nm. In this study, the thermal conductivity for different average grain sizes was calculated using the formula given by Nan et al \([31]\) which showed a good agreement with the experimental data. Another model named crowding factor model was employed by Rajasekar et al \([32]\) to evaluate the effective thermal conductivity of Si/Al doped \(\beta\)-Fe\(_2\)S\(_3\) composite as a function of average particle size. Here the model-based calculated \(k\) values for different average particle size were compared against the experimentally determined \(k\) values for corresponding particle size. With increase in the average particle size from 106 nm to 186 nm, the calculated \(k\) value increased from 11.7 W mK\(^{-1}\) to 13.1 W mK\(^{-1}\) while the experimental value shifts from 11.3 ± 0.6 W mK\(^{-1}\) to 13.4 ± 0.5 W mK\(^{-1}\). From the above result, it was evident that the predicted \(k\) values are in reasonable agreement with the experimental results. Although many studies have attempted to significantly increase the \(ZT\) value by grain refinement \([3, 25, 33]\), there is scope for further improvement by controlling or understanding the issues related to impurity concentration \([34]\), grain size distribution, and grain growth \([35]\) during fabrication by sintering etc.

In general, for structural property correlations, the microstructures are described by a single parameter such as an average grain size or average interlamellar spacing etc. For example, increase in hardness or strength due to grain size refinement is understood by plotting the strength against the inverse of the square root of the average grain size of the microstructure. Although this approach has found success in describing structure–property correlations, the distribution of the microstructural parameter cannot be completely overlooked. Ghosh et al \([36]\) demonstrated the effect of grain size distribution on the steady state creep behavior of superplastic aluminum and titanium alloys. Phaniraj et al \([37]\) invoked grain size distribution as an important microstructural parameter to explain the plastic flow and failure behavior of nanocrystalline materials. Similarly, Gollapudi \([38]\) investigated the effect of grain size distribution on corrosion behavior of magnesium in
both passivating and non-passivating medium. The study [38] revealed that for same average grain size, a microstructure with a broader grain size distribution is less corrosion resistant compared to that bearing a narrow grain size distribution in a passivating environment and vice versa for an active electrolyte. In a recent study, Gollapudi and Soni [39] have predicted that the concentration of the solute element segregating at the grain boundaries of a nanocrystalline microstructure is also a function of the grain size distribution. The above-mentioned studies have demonstrated that grain size distribution can be an important design parameter for the development of materials with superior properties.

In principle, the grain size distribution is expected to have an effect on thermal conductivity in all those materials which demonstrate a grain size dependence of thermal conductivity [40–42]. Experimental evidence for effect of grain size distribution on thermal conductivity has been provided by Gendelman et al [43]. Gendelman et al conducted some studies to establish the correlation between the width of the distribution and $k$ of copper and found that a broadening of the distribution leads to increase of $k$. However, there are very few systematic studies correlating the grain size distribution to thermal conductivity [43].

In this study, our objective is to check the effect of grain size distribution on the thermal conductivity of thermoelectric materials, which in turn can highlight its effect on the figure of merit $ZT$ of thermoelectric materials. In the following sections, we describe the approach taken and the results obtained from the exercise.

### 2. Problem formulation

We use the log normal distribution to describe the microstructure of the thermoelectric material. This is in line with the approach undertaken by Phaniraj et al [37] and Gollapudi [38]. The log normal distribution is given by the following equation:

$$f(d) = \frac{1}{\sqrt{2\pi}dS_n} \exp \left[ -\frac{1}{2} \left( \frac{\ln(d/d_M)}{S_n} \right)^2 \right]$$  \hspace{1cm} (2)

Where $d$ is the grain size, $S_n$ is the standard deviation in a number weighted grain size distribution and $d_M$ is the median grain size. The $d_M$ is further related to the average grain size, $d_{avg}$ as per the following equation [44].

$$d_M = \frac{d_{avg}}{(0.5S_n^2)}$$ \hspace{1cm} (3)

In order to check the effect of grain size distribution on thermal conductivity, we first need to establish the effect of grain size on thermal conductivity. As mentioned earlier, the thermal conductivity ($k$) of a material consists of two parts a. lattice thermal conductivity ($k_l$) and b. electronic thermal conductivity ($k_e$). The dependence of $k_l$ on $d$ is described by Takashiri et al [26] in their work on nanocrystalline n-type Bi$_2$Te$_3$ thin films. Takashiri et al [26] described the $k_l$ as a function of grain size using the theory of phonon scattering at grain boundaries [45, 46]. As per this theory, an increase in the number of grain boundaries leads to more phonon scattering which reduces the $k_l$ value. For a grain size too larger than the phonon mean free path, the dependence of $k_l$ on $d$ is given by

$$k_l = k_{iso} - \frac{2}{3}k_0 \sqrt{l_1 \frac{d}{3d}}$$ \hspace{1cm} (4)

Where $k_{iso}$ is the lattice conductivity of the material for negligible boundary scattering, $k_0$ is the lattice conductivity in the absence of alloy scattering and $l_1$ is the phonon mean free path. On the other hand, for a grain size comparable or smaller than phonon mean free path, the dependence of $k_l$ on $d$ is described by

$$k_l = \left( \frac{2k_0}{3} \right) \left[ \left( \frac{3d}{l_1} \right) \left( \frac{k_{iso}}{2k_0} \right) \right]^{3/4}$$ \hspace{1cm} (5)

In the above equations (4) and (5), the values of $k_{iso}$, $l_1$, and $k_0$ are observed to be different for different thermoelectric material. For Bi$_2$Te$_3$, these constants bear different values in the basal plane and along $c$-axis as its crystal structure is trigonal. Consequently, the $k_l$ is found to exhibit similar values in the $a$-axis and $b$-axis of the basal plane and but different values along the $c$-axis. The value of $k_l$ along the $a$-axis and $b$-axis, which are part of the basal plane, is similar while the $k_l$ along the $c$-axis is different to that of the $a$ and $b$-axis. Takashiri et al also demonstrated that the value of $k_l$ along $a$-axis and $b$-axis is the upper bound and the value of $k_l$ along $c$-axis is the lower bound for a given material. As a result, all the $k_l$ values estimated for Bi$_2$Te$_3$ from experiments falls within the theoretically calculated upper and lower bounds [24–26]. Similarly, dependence of $k_l$ with grain size for n type PbTe can also be calculated using equations (4) and (5). In the case of PbTe, due to its cubic structure, the same values of the parameters $k_{iso}$, $l_1$, and $k_0$ can be used for $a$-axis, $b$-axis and $c$-axis.
In order to understand the grain size dependence of $k$, it is important to know the grain size dependence of both $k_l$ and $k_e$ on $d$. The grain size dependence of $k_l$ is given by equations (4) and (5). However, the grain size dependence of $k_e$ has not been described in literature. In order to establish the same, the $k_e$ vs $d$ values reported for n type Bi$_2$Te$_3$ and n type PbTe are taken from literature [24, 26, 47, 48]. A linear fit was found to describe the dependence of $k_e$ on $d$, with an increase in $d$ leading to increase in value of $k_e$. By combining the $k_e$ and $k_l$ dependence on $d$, the dependence of $k$ on $d$ is determined. This correlation is then used for determining the effect of grain size distribution on $k$. Since in a distribution, there will be different grain sizes with each grain size having a certain frequency of occurrence, the contribution of each grain size to the thermal conductivity of the distribution is found using the weighted average method. The frequency of occurrence $f(d)$ is a function of $S_w$ through equation (2) and by varying the $S_w$, the $f(d)$ is varied which in turn changes the weighted contributions of the different grain sizes to the total $k$. In this way the effect of $S_w$ on $k$ is determined.

In addition to determining the variation of $k$ with $S_w$, we attempt to understand the effect of a bimodal grain size distribution on $k$ value by using the Bi$_2$Te$_3$ as a case study. This is necessitated by the observations of Zhao et al [49]. In order to optimize the value of ZT, Zhao et al [49] synthesized a bimodal microstructure which had a mixture of both coarse and fine grains. The material with the bimodal microstructure was created by mixing powders of different grain sizes and processed into bulk forms by spark plasma sintering method. The material under discussion, consisted of 100 nm and 1 $\mu$m sized Bi$_2$Te$_3$ grains and the highest value of ZT was obtained for a microstructure bearing 60% by weight of fine particles. This work by Zhao et al highlights the importance of a bimodal microstructure and as part of this study, we investigate the effect of $S_w$ on $k$ for a bimodal microstructure.

### 3. Results and discussions

In line with the approach described earlier, we first plot the variation of $k_l$ with $d$ using equations (4) and (5) for both n type Bi$_2$Te$_3$ and n type PbTe at 300 K. As mentioned before, the values of the parameters required in equations (4) and (5) for n type Bi$_2$Te$_3$ are taken from Sharp et al [50] and these values are also reported in table 1. Using these, the upper and lower bounds of $k_l$ for different values of $d$ is plotted in figure 1(a). Similar to the observations of Takashiri et al [25], figure 1(a) reveals an initial steep rise in the value of $k_l$ with $d$. However, it
seems to taper off at grain sizes greater than 1 \( \mu m \). This behavior is replicated by both the lower and upper bounds of \( k_l \). Similarly, the values of the parameters for n type PbTe are reported in table 2 with appropriate references. The variation in \( k_l \) value with grain size for PbTe can be seen from figure 1(b). In both the cases, stabilization of \( k_l \) values at higher grain size can be seen. The stabilization of \( k_l \) at higher \( d \) values can be understood from the fact that with increase in grain size, the grain boundary fraction of the material reduces significantly. The dependence of grain boundary fraction, \( f_{gb} \), on grain size, \( d \), is given by equation (6)

\[
f_{gb} = 1 - \left( \frac{d - t}{d} \right)^3
\]

Where \( t \) is the grain boundary thickness which is generally assumed as 0.5 nm [51]. Figure 2 shows the variation of grain boundary fraction of a microstructure as a function of grain size and reveals that at grain sizes larger than 1 \( \mu m \), the grain boundary fraction is very small and invariant of the grain size of the material. As grain boundaries with their inherent disorder are known to reduce thermal conductivity, a constancy of grain boundary fraction at large grain sizes indicates that the dependence of lattice thermal conductivity on grain size would reduce at larger grain sizes which is what is suggested by figure 1.

By gathering data from literature, we estimated the variation of \( k_s \) with grain size for both Bi\(_2\)Te\(_3\) & PbTe and the same is shown in figures 3(a) and (b) respectively. A linear fit is found to describe the variation of \( k_s \) with \( d \) with increase in grain size leading to increase in \( k_s \) values. Since we could not find information on \( k_s \) at very high grain sizes such as 10 \( \mu m \) and more, it is not clear if \( k_s \) will continue to increase with grain size or if it would become independent of \( d \) for coarse grain sizes. Based on the available data gathered from literature, we find that \( k_s \) increases linearly with \( d \) up to a grain size of 4 \( \mu m \), beyond which it might stay constant or increase at a lower rate considering that \( f_{gb} \) becomes very low for grain sizes greater than 1 \( \mu m \) and more.

Since the thermal conductivity \( k \) is a sum of \( k_l \) and \( k_s \), the dependence of \( k \) on \( d \) can be obtained by summing the individual dependencies of \( k_l \) and \( k_s \) on \( d \). The dependence of \( k \) on \( d \) for Bi\(_2\)Te\(_3\) & PbTe are shown in figures 4 and 5. It is interesting to note that the rate of increase of \( k \) with \( d \) is initially low for both the cases. This behavior is observed up to a grain size of 100 nm. However, after 100 nm, the value of \( k \) starts increasing rapidly with \( d \). This behavior of \( k \) can be understood from the fact that unlike \( k_l \) which increases rapidly with grain size even at \( d < 100 \) nm, \( k_s \) does not undergo a significant change with \( d \) up to 100 nm. Consequently, \( k \) undergoes a slow change with \( d \) in the nanocrystalline regime.

Table 2. Parameters used for calculation of lattice thermal conductivity of n type PbTe.

| Parameters | Value | References |
|------------|-------|------------|
| \( k_0 \) (W mK\(^{-1}\)) | 2.98 | [52] |
| \( k_s \) (W mK\(^{-1}\)) | 2.05 | [53] |
| \( l_t \) (m) | \( 3.4 \times 10^{-8} \) | [5] |

Figure 2. Variation of grain boundary fraction, \( f_{gb} \), with grain size, \( d \).
Figures 4 and 5 provides the variation of $k$ with $d$ for different values of $S_n$ for Bi$_2$Te$_3$ and PbTe respectively. It is apparent from figures 4(a) and 5(a) that an increase in $S_n$ leads to a reduction in the $k$ value and this effect is more so at intermediate grain size values. At lower grain sizes such as 20 nm, the $k$ values are not changed significantly by a change in $S_n$ and the same is observed for grain sizes greater than 1 $\mu$m. Figures 4(b) and 5(b) provides a magnified view of the $k$ values at intermediate grain size values and it is clear that an increase in $S_n$ causes a greater reduction in $k$ compared to the reduction observed for very fine or very coarse grains. This dependence is better illustrated by figures 6 and 7 wherein we have plotted the reduction in $k$ for Bi$_2$Te$_3$ and PbTe respectively, $\Delta k$ as a function of $S_n$ for different grain sizes. The $\Delta k$ corresponds to a reduction in $k$ when evaluated with respect to the $k$ value at $S_n = 0$. Figure 6(a) describes this change for the upper bound of $k$ and figure 6(b) describes this change for the lower bound of $k$ for Bi$_2$Te$_3$. Similarly, figure 7 depicts this change in $k$ for PbTe. It is interesting to note that $\Delta k$ increases with $S_n$ irrespective of the grain size. However, this increase in $\Delta k$ with $S_n$ is higher for microstructures with average grain sizes in the range of 100 nm and 1 $\mu$m and lower for the very fine ($d < 100$ nm) and coarse grained ($d > 1$ $\mu$m) microstructures. The values of $\Delta k$ for Bi$_2$Te$_3$ for the upper and lower bounds of $k$ are shown in tables 3(a) and (b) respectively. These values were used for making the figures 6(a) and (b). The values of $\Delta k$ for PbTe are shown in table 4 and used for constructing figure 7.
The key takeaways from this analysis is that

1. An increase in grain size, \( d \), leads to an increase in \( k \). This is understood from the fact that with an increase in \( d \), there is a reduction in the number of grain boundaries which are essential for phonon scattering. Consequently, this leads to an increase in the thermal conductivity.

2. An increase in the distribution width, \( S_n \), can lead to a reduction in \( k \) for all microstructures. Except for the work by Gendelman et al [43], there have been no works correlating grain size distribution to \( k \). Our observations on the correlation between \( S_n \) and \( k \) are contrary to the observations of Gendelman et al. One possible reason for this difference is that in addition to number of grain boundaries, the nature/type of the grain boundaries such as tilt boundaries, twist boundaries, coincident site lattice (CSL) boundaries will also affect the thermal conductivity. Gendelman et al [43] did not conduct a thorough characterization of the grain boundary character and hence a direct comparison with their work is not proper.

3. This reduction in \( k \), \( \Delta k \), was observed to be higher for the intermediate grain sizes instead of the fine (\( d < 100 \text{ nm} \)) or coarse grained (\( d > 1 \mu \text{m} \)) microstructures. This can be understood from figures 1(a) and (b). The change in \( k_\theta \) with \( d \) occurs at a higher rate in the intermediate grain size (100 nm < \( d < 1 \mu \text{m} \)) region compared to the finer and coarser grained regions. As a result, effect of \( S_n \) on \( k \) is more pronounced in
the intermediate grain size regions. On the other hand, the change in $k$ with $d$ occurs with a constant slope irrespective of the grain size in this range. Thus, a combination of $k_e$ and $k_l$ experiences the effect of $S_n$ only in the intermediate grain size region.

**Table 3.** (a): Decrease in thermal conductivity (Upper bound) for Bi$_2$Te$_3$; (b): Decrease in thermal conductivity (Lower bound) for Bi$_2$Te$_3$.

| $d$ | $S_n = 0$ | $S_n = 0.2$ | $S_n = 0.5$ | $S_n = 0.75$ | $S_n = 1$ |
|-----|-----------|-------------|-------------|-------------|-----------|
| (a) |           |             |             |             |           |
| 20 nm | 0        | 0.88        | 8           | 19.5        | 36.6      |
| 100 nm | 0       | 2.02        | 20.49       | 48.12       | 79.6      |
| 400 nm | 0       | 3.05        | 20.77       | 47.66       | 84.75     |
| 600 nm | 0       | 9.17        | 32.68       | 66.94       | 110.93    |
| 1 μm | 0 | 4.26 | 26.5 | 53.2 | 98.3 |
| 3 μm | 0 | 1.8 | 16.7 | 32.4 | 37.6 |

**Table 4.** Decrease in thermal conductivity for PbTe.

| $d$ | $S_n = 0$ | $S_n = 0.2$ | $S_n = 0.5$ | $S_n = 0.75$ | $S_n = 1$ |
|-----|-----------|-------------|-------------|-------------|-----------|
|     |           |             |             |             |           |
| 20 nm | 0        | 3.5         | 21.6        | 50.9        | 94        |
| 100 nm | 0       | 5.2         | 52.3        | 123         | 203.4     |
| 400 nm | 0       | 5          | 31.5        | 83.4        | 158.3     |
| 600 nm | 0       | 4.1         | 26.4        | 65          | 126.6     |
| 1 μm | 0 | 3.2 | 21.6 | 53.7 | 104 |
| 3 μm | 0 | 1.4 | 12.8 | 24.7 | 30 |

**Figure 7.** Reduction in $k$ for PbTe as a function of standard deviation $S_n$ and grain size $d$. 
Although grain sizes of the order of 10–20 nm provide very low \( k \) values, retaining of these grain sizes may be challenging while making bulk thermoelectric parts using the powder processing route. The grains of the mechanically milled powder would typically grow to larger sizes during conventional sintering or advanced sintering techniques such as spark plasma sintering. In such cases, the increase in \( k \) brought about by an increase in \( d \) can be circumvented if the microstructure bears a high \( S_n \). For example, in figure 5(b), it can be observed that a microstructure with an average grain size of 100 nm and a \( S_n \) of 0.2 bears the same \( k \) value as that of a microstructure with an average grain size of 200 nm and a \( S_n \) value of 1. This implies that it is not mandatory to have very fine grain sizes to achieve a low value of \( k \) as long as the grain size distribution is kept broad.

Generally, the beneficial effects of grain size distribution are demonstrated by materials bearing bimodal microstructures. Wang et al\[54\], demonstrated a good combination of high strength and ductility in copper bearing a mixture of nanocrystalline and coarse grains. Similarly in thermoelectric materials, Zhao et al\[49\] demonstrated that it is possible to tailor the \( ZT \) by developing a bimodal microstructure. Other studies such as\[55–58\] also investigated the \( k \) in bimodal microstructure. In the current study, we have made an attempt to describe the effect of \( S_n \) in a bimodal microstructure using Bi\(_2\)Te\(_3\) as a case study. The bimodal microstructure simulated for our study is shown in figure 8. It has two major components. One component bears an average grain size of 20 nm and the other component bears an average grain size of 1 \( \mu \)m. It is possible to modify the volume fraction of the fine and coarse grain sizes and study the effect of both volume fraction and \( S_n \) on \( k \). This study as mentioned earlier is essential as Zhao et al\[49\] already reported the benefits of using a bimodal microstructure on \( k \) and \( ZT \). With this in mind, the thermal conductivity values are being calculated by treating each grain size distribution independently and then adding their contributions using the rule of mixtures. In this way, the total thermal conductivity becomes a function of \( S_n \) of the distribution and the volume weighted fraction of constituent parts.

Figure 9 shows the effect of both volume fraction and \( S_n \) on the value of \( k \). The figure reveals that there is an enhancement in the value of \( k \) as the volume fraction of the coarse grains is increased. This is easily understood from the fact that an increase in volume fraction of the coarse grains leads to a reduction in the number of grain boundaries and consequently a reduction in the number of barriers to thermal conductivity. The figure also allows us to understand the effect of \( S_n \) of the two components of the bimodal microstructure on its thermal conductivity. We study three different cases. In first case, the standard deviation of both the major components is kept same at 0.2. Here standard deviation of the fine grain component is addressed as \( S_{n1} \) and the standard deviation of the coarse grain component is addressed as \( S_{n2} \).

- First case, \( S_{n1} = S_{n2} = 0.2 \).
- Second case, \( S_{n1} = 0.2 \) and \( S_{n2} = 1 \)
- Third case, \( S_{n1} = 1 \) and \( S_{n2} = 0.2 \)

It can be seen from figure 9 that for low volume fraction (0.2 or lower) of coarse grains, the microstructure has the same \( k \) value irrespective of the \( S_n \) values of the finer and coarse grain fractions. At large volume fractions (0.4 and higher) of the coarse grains, the value of \( k \) for case 2 is found to be lower than that of case 1 and case 3.
This behavior is observed for both the upper bound and lower bound of $k$ values. This exercise reveals that in a bimodal microstructure, the effect of $S_n$ is not significant if the volume fraction of the coarse grains is small such as 0.2 or lower.

The key takeaway of the analysis on bimodal microstructure is that the effect of $S_n$ becomes significant only when the volume fraction of coarse grains is high and a lower value of $S_{n1}$ and a higher value of $S_{n2}$ will be more beneficial for the thermoelectric material. A small value of $S_{n1}$ will imply that the fine grain component would have a narrow distribution of grain size and since $k$ is small for fine grains, a small $S_{n1}$ ensures that the $k$ value is not increased. On the other hand, a large value of $S_{n2}$ will ensure that there will an increase in the number of fine grains contributing to the distribution. Since finer grains reduce $k$, an increase in their number brought about by an increase in $S_{n2}$ will lead to an overall lowering of $k$ which in turn will be beneficial for the ZT. Thus, a tailoring of $S_n$ can aid in the lowering of the $k$ value even for a bimodal microstructure.

4. Conclusion

1. The effect of grain size distribution, described by $S_n$ on the thermal conductivity $k$ was studied for thermoelectric materials. The thermoelectric systems Bi$_2$Te$_3$ and PbTe were chosen as there is a lot of data available in literature for this system.

2. In order to establish the effect of $S_n$, it was first necessary to identify the effect of grain size $d$ on the thermal conductivity. By using literature data, we developed a correlation for electronic thermal conductivity $k_e$ against $d$ and found a linear dependence with an increase in $d$ leading to an increase in $k_e$. This dependence of $k_e$ on $d$ was combined with the dependence of $k_l$ on $d$, already existing in literature, to obtain the dependence of $k$ on $d$.

3. It was found that thermal conductivity, $k$, increases with $d$. However, for the same average grain size, an increase in $S_n$ leads to a reduction of $k$. The reduction in $k$, $\Delta k$, with increase in $S_n$ is higher for microstructures with average grain size in the range of 100 nm and 1 $\mu$m.

4. The effect of $S_n$ on the thermal conductivity of bimodal microstructures was also studied by using data from Bi$_2$Te$_3$. It was observed that an increase in volume fraction of coarse grains increases the value of $k$. On the other hand, for a given volume fraction of coarse grains, a decrease in $k$ can be achieved if the $S_n$ of the coarse grains is high and the $S_n$ of the fine grains making up the bimodal microstructure is low.

Data availability statement

The data that supports the findings of this study are available from the corresponding author upon reasonable request.
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