Effect of nanoinclusions on the lattice thermal conductivity of SnSe

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Abstract

We theoretically investigate the effect of nanoparticle (NP) inclusion on the lattice thermal conductivity ($\kappa_l$) of SnSe matrix. The theoretical approach involves the prediction of $\kappa_l$ by varying the radius ($R$), density ($D_v$), and volume fraction ($\varepsilon$) of NP in SnSe matrix. NP has strong anisotropic effect on the lattice thermal conductivity reduction along the crystallographic direction. We observe the existence of an optimal NP volume fraction that minimizes the nanocomposite’s thermal conductivity. At room temperature, this value is found to be $\varepsilon = 0.317$ for which lattice thermal conductivity reduces by 35% with NP ($R = 5$ nm) compared to pure SnSe. An enhancement in the figure of merit ($ZT$) around room temperature opens up new opportunities for thermoelectric power generation at moderate temperatures. Even larger enhancement is possible in polycrystalline SnSe which will be helpful for thermoelectric devices.

1. Introduction

Sustainable energy storage and conversion by thermoelectric devices can be a vital technological response to the global energy crisis [1, 2]. Thermoelectric (TE) materials will play a key role in reducing the environmental pollution in an environment-friendly manner [3, 4]. Energy conversion efficiency of thermoelectric material is characterized by its figure of merit, $ZT = S^2\sigma T/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa$ is the total thermal conductivity, and $T$ is the absolute temperature.

Bulk and thin films of tin selenide (SnSe) have been widely studied for various applications such as memory switching devices, cathode materials in thin film polarizers, optoelectronic devices and as candidates for solar cell applications [5–7]. Recently SnSe has been seen as one of the most promising TE material due to its excellent energy conversion efficiency, low cost, and high earth abundance of the component elements [8, 9]. Ultralow lattice thermal conductivity of SnSe [8] has a major contribution on $ZT$ at high temperature. However, the $ZT$ of SnSe around room temperature is still low as compared to other materials [10, 11]. Overall performance of the devices can be improved if the $ZT$ around room temperature is enhanced.

While the electronic properties can be improved by doping and band convergence, thermal properties are well-tuned by nanostructuring, which has shown great promise to achieve high $ZT$ [12]. Nanoinclusions can reduce the thermal conductivity and improve power factor of the materials. The introduction of nanostructures increases the density of interfaces among embedded nanoparticles and host materials which act as scattering centers for phonons and reduce the lattice thermal conductivity ($\kappa_l$) due to the phonon-interface scattering [13–15]. $ZT$ enhancement has been found in various nanostructured material families, including Bi$_2$Te$_3$-based nanocomposites [16, 17], SiGe-based nanocomposites [18–20] and SnSe-based nanocomposites [21–24]. Protsak et al. [23] showed that nanocomposites combining tin selenide (SnSe) with graphene oxide (GO) improve the power factor by 8.6%. Another study [22] showed that the introduction of Au in SnSe changes the transport channel of carriers along the press direction due to the percolation effect, increasing electrical conductivity, and $ZT$ value ~0.72 is achieved. Huang, and Lu et al. [21] showed that thermoelectric performance of SnSe/rGO sintered pellets could be optimized by tuning the rGO mass fraction, with SnSe/rGO-0.3 achieving $\kappa_l = 0.36$ Wm$^{-1}$K$^{-1}$ at 773 K to yield a maximum $ZT$ of 0.91 at 823 K.

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In this study, the effect of nanoparticle inclusion on the lattice thermal conductivity of SnSe has been investigated. Nanoparticles of different sizes and densities are considered, and their impact is seen on the phonon scattering rate. An optimized value of volume parameter and density of the nanoparticle is found which reduces the lattice thermal conductivity. Thus, nanoparticle inclusion would enhance the ZT of SnSe at lower temperatures considerably.

2. Theoretical methods

To determine the effect of nanoparticle inclusion on the lattice thermal conductivity of SnSe(Pnma spacegroup), density functional theory (DFT) calculations are performed using the Vienna Ab-initio Simulation Package (VASP) based on the projector augmented wave method (PAW) [25, 26] and the Perdew–Burke–Ernzerhof (PBE) [27] approximation to the exchange and correlation terms of the functional. The cut-off energy for the plane wave basis is set to 336.29 eV with a $2 \times 5 \times 5$ k-mesh. The convergence threshold of $10^{-8}$ eV is set for the energy and 0.01 eVÅ$^{-1}$ for the forces. The phonon dispersion is then obtained using the Phonopy package [28], by calculating the harmonic force constants in a $2 \times 3 \times 3$ supercell through a finite-difference method by applying atomic displacements with an amplitude of 0.01 Å. Within the relaxation time approximation, the lattice thermal conductivity is calculated as [29, 30],

$$\kappa_l = \frac{1}{3} \sum_b \int \frac{d^3 q}{8\pi^3} \nu_{b,q}^2 \tau_{b,q} C_{b,q}$$

(1)

where the sum is over all phonon bands $b$, the integral is over all the Brillouin zone, $\nu_{b,q}$ is the group velocity of a given phonon mode, $\tau_{b,q}$ is the mode relaxation time and $C_{b,q}$ is the mode heat capacity, dependent on the mode frequency $\omega_{b,q}$ and temperature. The thermal conductivity equation represents a completely general result and is valid in case of anharmonic lattice vibrations also as all the phonon modes are considered. Except for the relaxation time, the quantities in the equation can be extracted directly from the phonon dispersion relation of the material. The phonon relaxation time is calculated considering anharmonic scattering by using Grüneisen parameter which is related to anharmonicity of individual phonons [30, 31]. As SnSe is a layered material, to avoid the overestimation of thermal conductivity, normal scattering is also included [9]. The relaxation times as mentioned are calculated following quasi-harmonic approximation [31]. The effect of the nano inclusion is added considering nanoparticle scattering. The total relaxation time then becomes a sum of anharmonic (umklapp - $\tau_u$ and normal - $\tau_N$) and nanoparticle - $\tau_{NP}$ scattering contributions.

$$\tau^{-1} = \tau_u^{-1} + \tau_N^{-1} + \tau_{NP}^{-1}$$

(2)

The relaxation time due to umklapp scattering is well described by [12, 31],

$$\frac{1}{\tau_u} = \rho \omega^9 \frac{T}{\Theta_D} e^{-\Theta_D/(3T)}$$

(3)

where $\rho$ is an adjustable parameter [12], $\Theta_D$ is the Debye temperature, $T$ is the temperature and $\omega$ is the phonon mode frequency. The normal scattering plays an important role for layered chalcogenides like SnSe and is given by [9, 32],

$$\frac{1}{\tau_N} = B_N \omega^4 T^b$$

(4)

where $B_N$ is the normal phonon scattering rate coefficient [9]. To include contribution of nanoparticles in the system, a fractional quantity $\varepsilon$ is defined which is the ratio of volume of nanoparticle to the total volume of system ($V_T$) when nanoarticle is included.

$$\varepsilon = \frac{V_{NP}}{V_T}$$

(5)

The contribution of the nanoparticles to the frequency dependent mean free path is included in relaxation time as [33],

$$\frac{1}{\tau_{NP}} = \nu \sigma \rho$$

(6)

where, $\rho = \frac{1}{V_T} = \frac{1}{\left(\frac{V_{NP}}{V_T}\right)}$ is the density of nanoparticles and $\sigma$ is the cross-section limit of the nanoparticles. $\sigma$ plays an important role in scattering due to nanoparticles, and for simplicity, the particles are considered spheres. The Mie solution [34, 35] depicted that when electromagnetic waves encounter spherical particles, the scattering cross-section varies from frequency-dependent long-wavelength Rayleigh regime to frequency-independent short-wavelength geometric regime. Kim and Majumdar [13] bridged the scattering cross-section of the two regimes and proposed the effective cross-section $\sigma$ using a Matthiessen type interpolation as,
where, $\sigma_l$ is the cross-section limit in the long wavelength regime and depends on the size parameter $\chi = \frac{w}{v}$ as [33],

$$\sigma_l = \frac{\pi R^2}{9} \left( \frac{\Delta D}{D} \right)^2 \chi^4$$

In the above equation, $R$ is the radius of the nanoparticle. This limit also depends on the mass difference between embedded and host materials, which is incorporated by the term $\Delta D/D$, where $\Delta D$ is the difference between the nanoparticle density ($D_1$) and SnSe matrix ($D$). At short wavelengths, $\chi \rightarrow \infty$ the scattering cross-section is independent of frequency, and [33] gives the cross-section limit

$$\sigma_s = 2\pi R^2$$

These scattering rates are employed together to give the lattice thermal conductivity ($\kappa_{SnSe+NP}$) of the system using equation (1). Thermal conductivity of NP ($\kappa_{NP}$) is also calculated using relaxation time approximation. Total thermal conductivity of a medium with nanoparticles can be modelled using the Landau and Lifshitz [36] relation for the thermal conductivity of heterogeneous materials as [37–42],

$$\kappa_l = (1 - \varepsilon) \kappa_{SnSe+NP} + (\varepsilon) \kappa_{NP}$$

### 3. Results and discussion

Figure 1 (a) shows the SnSe host matrix embedded with nanoparticle(NP). As $\varepsilon$ is a ratio of the volume fraction of nanoparticle and SnSe matrix, it has a maximum limit. The maximum value of $\varepsilon$ is (See figure 1(c)),

$$\varepsilon = \frac{4\pi R^3}{a^3} = 0.523 \quad (a = 2R)$$

Hence, $\varepsilon$ cannot cross 0.523. As seen from equation (8)–(10), the composite’s thermal conductivity depends largely on $\varepsilon$, radius of nanoparticle and the mass difference between embedded and host materials.

Figure 2(a) shows that the average lattice thermal conductivity ($\kappa_l = \frac{\kappa_{SnSe+NP} + \kappa_{NP}}{2}$) starts decreasing after a certain value of $\varepsilon$. This value is in order of $10^{-3}$ for $R < 10$ nm and $10^{-2}$ for $R < 50$ nm. A remarkable feature in figure 2(a) is the appearance of a minimum average thermal conductivity for a given radius at an optimal value of $\varepsilon = 0.317$. After this $\varepsilon$, for different nanoparticle inclusions as seen from equation (10), the nanoparticle’s thermal conductivity starts to play a role; as a result, the total $\kappa_l$ again starts rising. For a particular $\varepsilon$, $\kappa_l$ decreases with a decrease in nanoparticle size. Figure 2(b) shows that for a particular $\varepsilon$ and size of nanoparticle, a small decrease in $\kappa_l$ is seen with increase in mass difference between the SnSe matrix and nanoparticle. When the
A nanoparticle is small in size, the effect of mass difference is seen more. The difference in $\kappa_l$ becomes negligible as $(\Delta D/D) > 2$ for $R = 5$ nm and 20 nm. Experimental values for SnSe/Graphene-0.3 wt% [24], SnSe/Graphene-0.5 wt% [24] and SnSe/Au [22] nanocomposite are also shown.

The variation of $\kappa_l$ with $R$ for different $(\Delta D/D)$ parameter is shown in figure 3(a). For a fixed value of $\varepsilon$, $\kappa_l$ decreases with size of the nanoparticle for different $(\Delta D/D)$. It is seen that nanoparticle inclusion considerably reduces the thermal conductivity of bulk SnSe. It is also observed that NPs have strong directional dependence in reducing thermal conductivity. Among the three crystallographic direction of bulk SnSe (See figure 1(b)), the lattice thermal conductivity is lowest along $a$-axis (orthorhombic direction) and NPs have minimum effect on this axis. Because along $a$-axis, smaller frequencies are mostly scattered by the anharmonic phonon scattering. However along $b$-axis and $c$-axis, NPs have intense effect in $\kappa_l$ reduction. Even very large NPs ($R > 100$ nm) can reduce lattice thermal conductivity along these axis by a factor of two. Therefore, the average lattice thermal conductivity can be tuned by inclusion of NPs in SnSe. This will be beneficial for the devices with polycrystalline SnSe where average thermal conductivity of all crystallographic direction is important.

A nanoparticle with $(\Delta D/D) > 2$, can be considered substantial to reduce the thermal conductivity of bulk SnSe. At 300 K (See figure 3(b)) with aforementioned parameter values, thermal conductivity of SnSe reduces by

**Figure 2.** Variation of lattice thermal conductivity with volume fraction parameter ($\varepsilon$) for different (a) size of the nanoparticle ($R$) and (b) mass difference parameter $(\Delta D/D)$. The experimental values for SnSe/Graphene-0.3 wt% [24], SnSe/Graphene-0.5 wt% [24] and SnSe/Au [22] nanocomposite are also shown.

**Figure 3.** Variation of lattice thermal conductivity of SnSe and SnSe/NP with (a) size of the nanoparticle ($R$) for $(\Delta D/D) = 0.1, 3$ and (b) temperature for $R = 5, 20$ nm.
35% on inclusion of nanoparticle. At higher temperatures, nanoparticle inclusion does not have much effect on \( \kappa \) due to the domination of anharmonic scattering. To understand the behavior of \( \kappa \), the variation of relaxation time with frequency due to different scattering mechanisms is plotted in figure 4(a). As seen from the figure, the total relaxation time is dominated by the umklapp scattering at higher frequencies. At lower frequencies, when \( \varepsilon \) is in order of \( \sim 10^{-2} \), the relaxation time is guided by normal scattering. When \( \varepsilon \) is increased to 0.317, the density of nanoparticles (\( \rho \)) increases, and as a result, nanoparticle scattering increases. Thus, nanoparticle scattering dominates the total relaxation time which leads to reduction of thermal conductivity. Figure 4(b) shows the variation of cross-section limits (\( \sigma \)) with \( \omega R \). As \( \sigma \) is frequency independent, it is the same for all frequencies, but increases with nanoparticle size. As seen from the inset plot, the total cross-section limit (\( \sigma \)) is dominated by \( \sigma_s \). As \( \sigma_s \propto R^4 \omega^4 \), it increases with the radius of nanoparticle as well as frequency. At lower frequencies when the nanoparticle is small in size (See figure 4(c)), the long-wavelength and short-wavelength cross-section limits become comparable and together affect the nanoparticle scattering rate. The limits have no variation with \( \varepsilon \).

Along with radius, interparticle distance (\( \delta \)) also plays an important role in reducing the composite’s lattice thermal conductivity. As seen from figure 1(c), the interparticle distance is defined as,

\[
\delta = 2(a - R) = 2R \left( \frac{a \varepsilon}{3\nu} \right)^{1/3} - 1.
\]

From the definition, \( \delta \propto R \left( \frac{1}{\varepsilon} \right)^{1/3} \); so when the nanoparticle size is kept fixed, say \( R = 5 \) nm, and \( \varepsilon \) parameter is increased from 0.317 to 0.532, the interparticle distance decreases from 13.6 nm to 10 nm. This decrease in \( \delta \) causes the thermal conductivity of the composite to rise. The reverse is seen when the nanoparticle’s size is reduced, keeping \( \varepsilon \) fixed as then the size of the SnSe matrix has to be reduced to keep the volume ratio constant.

4. Conclusion

In conclusion, the calculations presented in this work indicate that the lattice thermal conductivity of SnSe matrix nanocomposite can be reduced by increasing the volume fraction parameter (\( \varepsilon \)) to a particular value for optimal size of the nanoparticle. On nanoinclusion, for \( R = 5 \) nm and \( \varepsilon = 0.317 \), the lattice thermal conductivity of bulk SnSe reduces from 0.77 Wm\(^{-1}\)K\(^{-1}\) to 0.49 Wm\(^{-1}\)K\(^{-1}\) at 300 K which is a 35% reduction from its original value. Similar to the bulk lattice thermal conductivity, NPs in the SnSe has strong directional dependence. NPs are more effective along in-plane thermal conductivity reduction compared to the orthorhombic direction. This will be helpful to polycrystalline materials and will further increase the thermoelectric figure of merit around room temperature.

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Data availability

The data that support the findings of this study are available upon request from the authors.
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