Thermal conductivity of Mg$_2$Si$_{1-x}$Sn$_x$ nanowires synthesized using solid-state phase transformation of silicon nanowires

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Abstract

Recent studies have indicated that doping, alloying, interface-engineering and nanostructuring are some of the strategies useful for obtaining high power factors and low thermal conductivities in materials that are needed for the fabrication of highly efficient thermoelectrics. With the intent of experimentally demonstrating the use of these strategies for designing highly efficient thermoelectrics, our group has in the past reported a solid-state phase transformation strategy for converting silicon nanowires into Mg$_2$Si nanowires and Mg$_2$Si welded nanowire networks. In this paper, the phase transformation strategy is extended to obtain Mg$_2$Si$_{0.92}$Sn$_{0.08}$ nanowires from silicon nanowires. This report discusses not only the synthesis of Mg$_2$Si$_{0.92}$Sn$_{0.08}$ nanowires from silicon nanowires, but also demonstrates that it is possible to control their diameters using variations of the silicon nanowire diameters as a parameter. Moreover, thermal conductivities of the nanowire assemblies discussed in detail in this paper indicated that nanostructuring through the formation of Mg$_2$Si$_{0.92}$Sn$_{0.08}$ nanowires led to a drastic decrease in their thermal conductivities.

Introduction

Thermoelectrics, solid-state heat engines that convert thermal energy into electricity, may play an important role in the future portfolio of renewable energy technologies useful for reducing reliance on fossil fuels [1]. However, for the widespread terrestrial deployment of thermoelectric generators, the current low efficiencies of thermoelectric modules of about 6%–7% should be further enhanced [2–5]. Both theoretical and experimental studies over the last two decades indicated that strategies, such as nanostructuring of materials [1], resonant scattering [6], interface engineering [7], could be employed to optimize the Seebeck Coefficients (S), electrical conductivities and thermal conductivities (κ) of materials and thereby enhance the figure of merit, $zT$

\[
 zT = \frac{S^2\kappa}{k_B}
\]

of materials that directly dictates the heat-to-electricity conversion efficiencies of thermoelectric devices and modules [5, 8–12]. Despite these successes, the current champion thermoelectric materials with peak $zT \sim 1$, such as bismuth telluride (Bi$_2$Te$_3$), lead telluride (PbTe) silicon-germanium (SiGe) alloys, remain those that are composed of toxic, rare earth, and/or expensive elements [13–15]. Consequently, the search for materials with high $zT$ values that are composed of only inexpensive, earth abundant, and non-toxic elements is still underway [16, 17].

Magnesium silicide (Mg$_2$Si) has long been considered to be a promising alternative for mid-temperature (i.e., 400–800 K) thermoelectric applications, and a viable replacement for PbTe [18, 19]. In addition to the low toxicity, high thermal and mechanical stability, low density, and high relative abundance of component elements [18, 20], Mg$_2$Si exhibits many characteristics ideal for a thermoelectric material, including a relatively large effective mass, high charge carrier mobility, and low lattice thermal conductivity [21, 22]. Despite intense efforts over the past decade, however, the peak $zT$ values for Mg$_2$Si have remained close to 1 [18, 23].
Another non-toxic alternative to PbTe is magnesium silicide stannide (Mg$_2$Si$_{1-x}$Sn$_x$), a pseudobinary alloy composed of Mg$_2$Si and Mg$_2$Sn [20]. Not only is Mg$_2$Si$_{1-x}$Sn$_x$ lighter as desired in automotive applications of thermoelectrics (the density of PbTe is 8.16 g/cm$^3$, more than twice the density of Mg$_2$Si$_{1-x}$Sn$_x$, which is expected to be between the values of 1.88 g cm$^{-3}$ and 3.59 g cm$^{-3}$ that respectively correspond to the densities of Mg$_2$Si and Mg$_2$Sn) [24], but also less expensive (the cost of Mg$_2$Si$_{1-x}$Sn$_x$ at $4/kg is significantly lower than those of the state-of-the-art thermoelectric materials, such as Bi$_2$Te$_3$, PbTe, and SiGe, which respectively cost $110/kg, $81/kg, and $679/kg) [20]. In fact, LeBlanc et al reported a cost of <$1/W is associated with Mg$_2$Si$_{0.6}$Sn$_{0.4}$ for thermoelectric power generation in the mid-to-high temperature range and concluded that it is a highly promising thermoelectric material [25]. Mg$_2$Si$_{1-x}$Sn$_x$ has been consistently demonstrated to exhibit $zT$ values larger than 1 by several different authors over the last few years [26–28]. Furthermore, unlike Mg$_2$Si, Mg$_2$Si$_{1-x}$Sn$_x$ offers the ability to optimize $zT$ values at different temperatures through bandgap adjustment (or compositional variations) [29]. Consequently, compositional variations can be used to tune the temperatures at which peak $zT$ values are obtained in Mg$_2$Si$_{1-x}$Sn$_x$ [13], highly desirable in the fabrication of thermoelectric modules operating in the intermediate and high temperature ranges [30].

While bulk Mg$_2$Si$_{1-x}$Sn$_x$ exhibits promising thermoelectric properties, with peak $zT$ values as high as 1.7, a few theoretical studies predict improved thermoelectric performance in nanowires due to a further reduction of thermal conductivity [31, 32]. Here, alloying reduces thermal conductivity due to phonon scattering by atomic-scale defects [33], and nanostructuring reduces thermal conductivity via boundary scattering of phonons [33]. At the same time, single crystalline or highly oriented polycrystalline nanowires can prevent degradation of electrical conductivity and thereby may lead to improvements in the $zT$ values [34]. In highly oriented polycrystalline nanowires, individual crystallites within a nanowire exhibit a relatively small orientation mismatch [35], which can lead to the formation of low-angle grain boundaries that have been demonstrated to lead to a smaller reduction in charge carrier mobility relative to high-angle grain boundaries [34, 36].

Despite these advantages, published results of thermal conductivities in Mg$_2$Si$_{1-x}$Sn$_x$ nanowires and nanowire assemblies are non-existent. This is primarily attributable to the difficulty associated with preventing the oxidation of both magnesium and tin during attempts to synthesize nanowires of Mg$_2$Si$_{1-x}$Sn$_x$, especially using vapor-based approaches (e.g. chemical vapor deposition (CVD)) [37]. Both mechanical alloying and melt synthesis techniques, typically used for obtaining bulk Mg$_2$Si$_{1-x}$Sn$_x$, are not suitable for the synthesis of nanowires [20]. Previously, our group has successfully demonstrated a solid-state phase transformation approach for obtaining both polycrystalline and single-crystalline Mg$_2$Si nanowires from single-crystalline silicon (Si) nanowires [7, 37]. In the present work, the phase transformation approach has been extended for obtaining Mg$_2$Si$_{1-x}$Sn$_x$ nanowires from Si nanowires. In addition to the synthesis of Mg$_2$Si$_{1-x}$Sn$_x$ nanowires, the thermal conductivities of bulk nanowires assemblies with different nanowire diameters will be presented in this manuscript.

**Experimental methods**

Synthesis of Mg$_2$Si$_{1-x}$Sn$_x$ nanowires was achieved via solid-state diffusion between Mg$_2$Si nanowires and bulk Mg$_2$Sn powders. While Si nanowires served as the raw material for the formation of Mg$_2$Si nanowires, Mg$_2$Sn powders were prepared using commercially-available magnesium and tin powders. All the experimental steps involved in the synthesis of these materials are detailed below. For each and every composition, a minimum of 3 samples have been prepared and studied for their thermoelectric performances to ensure the reproducibility of the results.

For the synthesis of Si nanowires in array form, metal-assisted chemical etching of boron doped (100)-oriented Si wafers was employed. This procedure has been extensively described previously in the literature [38]. Post-synthesis etching of Si nanowires was performed in an aqueous solution of hydrofluoric acid and nitric acid at room temperature to obtain nanowires with different diameters [39]. As described in a previous publication by Vaddiraju and coworkers, Mg$_2$Si nanowires were synthesized via a solid-state reaction between the Si nanowire arrays and polished magnesium foils (99.95%, 0.05 mm thick; Solution Materials, LLC) at 400°C–430°C in a vacuum chamber operating at a pressure of 50–100 mTorr in the presence of hydrogen gas [7].

For the formation of Mg$_2$Sn powders, stoichiometric amounts of magnesium (∼20 + 100 mesh, 99.8%, Alfa Aesar) and tin powders (<4 μm, 99.8% trace metals basis, Millipore Sigma) were employed. The powders were manually ground in a mortar and pestle to obtain a homogenous mixture and the resulting mixture was placed in between two freshly polished magnesium foils. The foils containing the powder mixtures were then placed in between two boron nitride plates, and a ceramic weight (45 g) was placed on top of this entire assembly to ensure good contact between the foils and powder mixture. This experimental assembly was placed on a pyrolytic boron nitride heating plate inside a stainless-steel reactor and heated to 450°C using a heating rate of 20°C min$^{-1}$. Reaction between the powders was allowed to occur for 5 h under a vacuum of 50–100 mTorr in
the presence of hydrogen. The presence of hydrogen and the presence of excess magnesium (in the form of foils) together aided in preventing the oxidation of Mg₂Sn formed. The presence of excess magnesium also ensured that stoichiometric Mg₂Sn is formed even upon some loss of magnesium due to evaporation over the course of the experiments.

Synthesis of Mg₂Si₁₋ₓSnₓ nanowires was finally achieved via solid-state diffusion between Mg₂Si nanowires and bulk Mg₂Sn powders. For accomplishing this task, pre-synthesized Mg₂Si nanowire powders and pre-synthesized Mg₂Sn powders were both separately ground and sieved using a sieve of pore size 0.0041” (or 106 μm) made according to ASTM E-11 specifications. The resulting Mg₂Si nanowire powders and the Mg₂Sn powders were mixed in stoichiometric amounts in an agate mortar and pestle. Finally, 10 wt.% excess magnesium powder was added to the resulting mixture to compensate for any loss of magnesium by evaporation during the ternary Mg₂Si₁₋ₓSnₓ synthesis process. The sieving step ensured that large chunks (or agglomerates) Mg₂Si nanowires and Mg₂Sn powders, which may potentially hinder interdiffusion and the formation of Mg₂Si₁₋ₓSnₓ, nanowires of uniform composition, are removed. The resulting mixture was then cold pressed using a graphite-lined stainless-steel die set at 365 MPa. The consolidated powder together with the die set was loaded into a vacuum chamber and allowed to react for 2 h at 750 °C and under a pressure of 100 mTorr in the presence of hydrogen. Presence of a reducing atmosphere of Hydrogen aided in minimizing oxidation of Mg₂Si and Mg₂Si₁₋ₓSnₓ, which have been reported to oxidize in air at 465 °C [40] and 430 °C [41], respectively.

For obtaining thermal conductivities of the Mg₂Si₁₋ₓSnₓ nanowire assemblies, pellets were prepared using the procedure below. Mg₂Si₁₋ₓSnₓ nanowires obtained using the above-mentioned procedure were crushed using a mortar and pestle, then loaded into a custom-built low carbon steel die lined with graphite, and consolidated at 420 °C and a pressure of 350 MPa for 2 h into a cylindrical pellet with a diameter of 12.7 mm and a thickness of 1 mm.

For comparison purposes, polycrystalline Mg₂Si₁₋ₓSnₓ was also synthesized in a similar manner. The only difference here is that crushed Si powders were used as the starting material, instead of Si nanowires. The density of pellets was measured via the Archimedes method in an ethanol medium (ethanol absolute ≥99.5% ACS (200 Proof)) [10]. Thermal diffusivity of the synthesized samples was measured via laser flash analysis under nitrogen flow (TA Instruments DLF 1200) while phase analysis was performed via powder x-ray diffraction (XRD, Bruker-AXS D8 Advanced Bragg-Brentano x-ray Powder Diffractometer) using Cu Kα radiation (40 kV, 25 mA). Field emission scanning electron microscopy (FE-SEM, JEOL JSM-7500F) was used to characterize the microstructure of fabricated samples.

**Results and discussion**

Metal-assisted chemical etching of Si wafers led to the formation of single-crystalline Si nanowire arrays (figures 1(a) and (b)), as previously reported by our group [7]. The electron microscopy images shown in figures 1(a) and (b) reveal that the nanowires had an average diameter of 101 nm (a histogram of the diameter distribution is provided in figure 1(c)) and an average length of 20 μm. Solid-state reaction between Si nanowires and Mg resulted in the formation of Mg₂Si nanowires, as seen in the SEM images in figures 1(d) and (e). The reaction between Mg and Si nanowires preserved the nanowire morphology, as previously reported [7]. The average diameter of the nanowires increased to 180 nm (a histogram of the diameter distribution is provided in figure 1(f)) upon conversion of Si to Mg₂Si. Finally, SEM images of the synthesized Mg₂Si₁₋ₓSnₓ, shown in figures 1(g) and (h), clearly depict the retention of nanowire morphology following solid-state diffusion between Mg₂Si nanowires and bulk Mg₂Sn. The final average diameter of the nanowires was observed to be 185 nm (a histogram of the diameter distribution is provided in figure 1(i)). Additional images of the Mg₂Si₁₋ₓSnₓ nanowires are provided in figure S1 of the supplementary information provided.

Theoretical calculations indicate that Si nanowires’ diameters increase by 1.78 times upon phase transformation to Mg₂Si (assuming that the length of the nanowires remains unchanged, and volume expansion leads to only diameter increase [37]). This agrees well with the observed changes in the average diameters of the Si and Mg₂Si nanowires from the above-described experimental data. To determine value of x in the Mg₂Si₁₋ₓSnₓ nanowire samples, similar analysis was performed. The final average diameter of 185 nm of the Mg₂Si₁₋ₓSnₓ nanowires indicates a volume expansion of 248% relative to the original diameter of the Si nanowires. Based on this estimation, the value of x was preliminarily determined to be 0.08. The latter estimate relies on keeping the number of silicon atoms constant in both the silicon nanowires and Mg₂Si₀.92Sn₀.08 nanowires, and estimating the volume occupied by silicon atoms when they are present in silicon crystalline form and Mg₂Si₀.92Sn₀.08 crystalline form. Diameter change could then be calculated by assuming that volume change primarily appears as a diameter change and expecting that the lengths of the nanowire remain unchanged upon phase transformation [37].
XRD analysis of the nanowires was then performed to confirm the composition of the ternary nanowires. XRD analysis of the as-obtained Si nanowires, along with those of the Mg$_2$Si nanowires and the Mg$_2$Si$_{1-x}$Sn$_x$ nanowires, are shown in figure 2. XRD analysis of Si nanowires (figure 2(a)(i)) confirms the absence of impurity phases, such as silver residue, in the nanowires (from the silver nitrate-based metal-assisted etching process used for Si nanowire synthesis). The XRD analysis of the Mg$_2$Si nanowires (figure 2(b)(ii)) clearly indicates the presence of a single Mg$_2$Si phase that is devoid of any impurities. While MgO peaks do not appear in the XRD pattern, the formation of MgO is extremely difficult to avoid as the reaction of Mg with Si native oxide leads to the formation of MgO on the surfaces of Mg$_2$Si nanowires [42]. In fact, TEM analysis from a previous report by Kang and co-workers indicates the presence of an MgO sheath on the Mg$_2$Si nanowires [7, 37].

Rietveld analysis of the XRD pattern of Mg$_2$Si$_{1-x}$Sn$_x$ (figure 2(a)(iii)) (details of the refinement can be found in the description of figure S2 of the supplementary information provided (available online at stacks.iop.org/MRX/8/025005/mmedia)) indicated that the lattice parameter of the nanowires, a, was 6.3737 Å. As the lattice parameters of Mg$_2$Si and Mg$_2$Sn are 6.338 Å and 6.765 Å, respectively [20], and Mg$_2$Si$_{1-x}$Sn$_x$ has been demonstrated to obey Vegard’s law [43], the composition of the ternary phase was estimated using the following equation [44]:

$$a = 6.338 + 0.427x.$$  

The calculation indicates that the composition of the as-synthesized material is in reasonably good agreement with that obtained through the analysis of the nanowire diameters from the SEM analysis explained above, and that the composition of the nanowires is Mg$_2$Si$_{0.92}$Sn$_{0.08}$ (i.e., x = 0.08). Mg$_2$Si$_{1-x}$Sn$_x$ is a pseudobinary alloy, i.e., a solid solution of the two binary compounds Mg$_2$Si and Mg$_2$Sn. As such, it can be thought of as a solution of one compound in the other, with the final alloy composition determining the identity of the solvent and solute compounds. However, since the percentage of Mg is held constant in these alloys, the solid solution is formed due to the interdiffusion of Sn and Si atoms between the crystal lattices of the binary compounds, both of which crystallize in the antifluorite crystal structure [20]. There has been considerable discussion in the literature over the miscibility gap of these two compounds and several reports in the literature have provided different values for the limits of the miscibility gap depending on synthesis conditions [20, 43]. Nevertheless, recent papers in the literature refer to the phase diagram published by Viennois et al to determine solid solution composition and processing temperature for the synthesis of Mg$_2$Si$_{1-x}$Sn$_x$ [43]. Furthermore, Gorsse et al have successfully demonstrated the formation of a series of single-phase solid solutions in the interdiffusion zone between Mg$_2$Si and Mg$_2$Sn via diffusion coupling, providing evidence for the presence of miscible solid solutions at various compositions, including the approximate

![Figure 1. SEM images of (a) and (b) as-synthesized Si nanowires, (d) and (e) Mg$_2$Si nanowires, and (g) and (h) Mg$_2$Si$_{1-x}$Sn$_x$ nanowires. The SEM images indicate that bending occurs in the binary and ternary nanowires due to the stresses associated with the large volume expansions during phase transformation. (c), (f) and (i) Histograms depicting the diameter distributions of as-synthesized Si nanowires, Mg$_2$Si nanowires, and Mg$_2$Si$_{0.92}$Sn$_{0.08}$ nanowires, respectively. Calculated average diameters along with standard errors are: 101 ± 7 nm for Si nanowires, 180 ± 12 nm for Mg$_2$Si nanowires, and 185 ± 8 nm for Mg$_2$Si$_{0.92}$Sn$_{0.08}$ nanowires.](image-url)
composition obtained in this work [45]. Finally, more recent reports by Sizov et al and Yasseri et al on detailed phase separation behavior in Mg2Si1−xSnx confirm that the composition obtained in this work is in fact in the single-phase region [46, 47]. Based on these results, it can be concluded that solid-state inter-diffusion between Mg2Si nanowires and bulk Mg2Sn leads to the observed formation of single-phase Mg2Si0.92Sn0.08 nanowires at the selected miscible composition in this work. In the bulk, foreign-atom diffusion that leads to large volume changes can cause a loss of morphology of the crystals [48]. The volume of a single Si nanowire should increase by approximately 248% upon transformation to Mg2Si0.92Sn0.08. As Si nanowires have been demonstrated to retain their morphology even for volume expansions as high as 400%, it is not surprising that nanowire morphology is retained when Si nanowires were phase transformed to Mg2Si0.92Sn0.08 nanowires [48].

To deduce the effect of nanowire diameters on the thermal conductivities of nanowire assemblies, Mg2Si0.92Sn0.08 nanowires of three different average diameters, 185 nm, 150 nm and 118 nm, have been synthesized and assembled into pellets. For accomplishing this task, diameters of the as-obtained silicon nanowires employed for phase transformation into Mg2Si0.92Sn0.08 nanowires have been altered (see figure S3 in the supplementary information provided). Silicon nanowires of average diameters 101 nm, 81 and 64 nm were employed as the starting material for obtaining Mg2Si0.92Sn0.08 nanowires of diameters 185 nm, 150 nm and 118 nm. Thermal conductivities of both bulk and nanowire samples of Mg2Si0.92Sn0.08 were calculated using the following equation [49]: \( \kappa = \alpha \cdot C_p \cdot \rho \). Here, \( \alpha \) is thermal diffusivity, \( C_p \) is specific heat capacity, and \( \rho \) is density. Pycnometry measurements indicated that the nanowire assemblies (or pellets) exhibit densities \( \geq 93\% \) in all the cases. Since the pellets exhibit porosities <10%, the rule of mixtures has been used to correct for the effect of porosity on thermal conductivity as follows: \( \kappa_{\text{eff}} = (1 - P) \kappa_{\text{full}} \), where \( \kappa_{\text{eff}} \) is the effective thermal conductivity observed in porous samples, \( P \) is the porosity, and \( \kappa_{\text{full}} \) is the thermal conductivity of 100% dense samples, respectively [50]. The Dulong-Petit approximation was applied to obtain \( C_p \) for Mg2Si0.92Sn0.08 (see supplementary information) as it has been demonstrated to fall within accepted accuracy for Mg2Si-based materials in the literature [51, 52]. Temperature-dependent thermal conductivity of both bulk and nanowire samples of Mg2Si0.92Sn0.08 are shown in figure 3(a).

The thermal conductivities of all Mg2Si0.92Sn0.08 samples decreased with an increase in temperature. Furthermore, as expected, samples made of nanowires of thinner diameters exhibited lower thermal conductivities than and all nanowire samples exhibited lower thermal conductivities than those exhibited by bulk Mg2Si0.92Sn0.08 samples. Electrical conductivity measurements of the samples, coupled with estimation of electronic contributions to the total thermal conductivities, indicated that the major contribution to the total thermal conductivity came from lattice vibrations (see description relating to figure S4 in the supplementary information provided for thermal conductivity calculations). Based on these estimates, a plot showing variation of lattice thermal conductivity (\( \kappa_l \)) with temperature was obtained as shown in figure 3(b). According to the figure, the temperature dependence of lattice thermal conductivity for both bulk and nanostructured Mg2Si0.92Sn0.08 samples is less than T−1, which indicates that alloy and Umklapp scattering of phonons are the dominant scattering mechanisms in the measured temperature range [44, 53–57]. The deviation of the lattice

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**Figure 2.** (a) XRD patterns of (i) as-synthesized Si nanowires, (ii) Mg2Si nanowires, and (iii) Mg2Si1−xSnx nanowires, and (b) XRD pattern of the (220) peak reflections indicating a down shift of the (220) peak reflection in the Mg2Si1−xSnx nanowires relative to that of Mg2Si nanowires.
thermal conductivity from a power law dependence on temperature for the 185 nm sample beyond 473 K is due to the onset of sample cracking during measurement of thermal diffusivity (observed at the end of the measurement process). No such deviation is observed in the other samples.

Furthermore, the experimental room temperature $\kappa_1$ obtained for bulk Mg$_2$Si$_{0.92}$Sn$_{0.08}$ is in good agreement with that calculated by Li 

It is worthwhile to note here that the thermal conductivity of bulk Mg$_2$Si$_{0.92}$Sn$_{0.08}$ samples is ~54% lower than experimental $\kappa_1$ for intrinsic bulk Mg$_2$Si reported by Tani et al. [31, 58]. Therefore, the result indicates that alloy scattering effectively reduces $\kappa_1$ in Mg$_2$Si$_{0.92}$Sn$_{0.08}$ relative to Mg$_2$Si. At 300 K, the 185 nm Mg$_2$Si$_{0.92}$Sn$_{0.08}$ nanowire sample has a $\kappa_1$ of 2.74 Wm$^{-1}$K$^{-1}$, which is ~43% lower than that of the bulk alloy sample. Reducing nanowire diameter to 150 nm lead to a $\kappa_1$ of 1.93 Wm$^{-1}$K$^{-1}$ at 300 K, 60% lower than that of bulk. However, a further reduction in nanowire diameter to 118 nm did not lead to a significant decrease in thermal conductivity. This can be understood by considering the fact that the phonons with mean free paths between 118 and 150 nm may not significantly contribute to the overall $\kappa_1$ in Mg$_2$Si$_{0.92}$Sn$_{0.08}$. A similar trend was previously reported for the Mg$_2$Si$_{0.6}$Sn$_{0.4}$ material system [31].

The reduction of $\kappa_1$ in the nanowire samples, relative to their bulk counterparts, is attributed to enhanced scattering of phonons. First and foremost, alloying has been demonstrated to dramatically lower the thermal conductivity in bulk Mg$_2$Si$_{1-x}$Sn$_x$ relative to Mg$_2$Si and the enhanced thermoelectric performance of Mg$_2$Si$_{0.92}$Sn$_{0.08}$ is largely attributed to such reduction in thermal conductivity [20, 24]. In such alloys, phonons are strongly scattered by atomic substitutions due to mass contrast and strain field fluctuations arising from size differences between the alloying and host atoms in the crystal lattice (i.e., disorder), which often leads to a significant reduction in thermal conductivity [33, 59, 60]. Secondly, the introduction of a relatively large number of grain boundaries resulting from the consolidation of as-synthesized Mg$_2$Si$_{0.92}$Sn$_{0.08}$ nanowires into macro-scale pellets also allows for reducing the thermal conductivity in these nanowire pellets, similar to that previously observed by our group with Zn$_3$P$_2$ and ZnO nanowire-based assemblies [6, 10, 11]. In fact, disorder in the system, such as a distribution of nanowire diameters in nanowire assemblies, aids in preventing coherent phonon scattering and allows for vastly reducing thermal conductivities in such nanowire assemblies. In periodic systems, such as superlattices, incoherent phonon scattering for reducing thermal conductivities of materials is partially masked by coherent phonon scattering [61, 62]. Hence, lowest possible thermal conductivities may not be achieved in superlattices [61, 62].

Modified Callaway model proposed by Bellanger et al was employed to estimate the theoretical thermal conductivities of the nanowire samples employed in this study. The calculations indicated that the model underestimates the impact of nanostructuring on lattice $\kappa_1$ of Mg$_2$Si$_{0.92}$Sn$_{0.08}$ (details of the model can be found in the supplementary information) [63]. The observed discrepancy between the model and experimental data may be attributed to the underlying assumption of a linear phonon dispersion in the original Callaway model and its modifications [64]. A more rigorous first-principles modeling may accurately predict the impact of nanostructuring on $\kappa_1$ of Mg$_2$Si$_{0.92}$Sn$_{0.08}$ [64].
Conclusions

Solid-state phase transformation was successfully employed to synthesize Mg$_2$Si$_{0.92}$Sn$_{0.08}$ nanowires from pre-synthesized Si nanowires and bulk Mg$_2$Sn powders. To vary the diameters of the Mg$_2$Si$_{0.92}$Sn$_{0.08}$ nanowires obtained through this strategy, the diameters of the Si nanowires used as one of the starting materials have been altered. Characterization of the resulting bulk nanostructured samples, obtained by uniaxially pressing nanowires into pellets, indicated that nanostructuring reduces lattice thermal conductivity in Mg$_2$Si$_{0.92}$Sn$_{0.08}$ below the alloy limit. A reduction of nanowire diameters to 118 nm led to a 60% reduction in the thermal conductivity of Mg$_2$Si$_{0.92}$Sn$_{0.08}$ relative to that exhibited by bulk Mg$_2$Si$_{0.92}$Sn$_{0.08}$. In short, the present study presents clear experimental evidence that nanostructuring through the formation of ternary compound nanowires of Mg$_2$Si$_{0.92}$Sn$_{0.08}$ could be employed in the design of efficient thermoelectrics.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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