1. Introduction

With the advent of efficient materials, thermoelectric (TE) power generation technology is gradually evolving as a suitable solution to harvest wasted heat energy sources.\[1\] The performance of a TE material is mainly judged by its dimensionless figure of merit (\(ZT\)) defined as \(ZT = S^2 \sigma T / (\kappa_e + \kappa_L)\), where \(S\), \(\sigma\), and \(T\) are the Seebeck coefficient, electrical conductivity, and absolute temperature, respectively, while \(\kappa_e\) and \(\kappa_L\) are the electronic and lattice contributions to the thermal conductivity. A powerful strategy towards higher \(ZT\) is to lower lattice thermal conductivity \(\kappa_L\) in which various methods, such as nanostructural engineering,\[2-5\] alloying (introducing mass and size disorder),\[6-8\] and constructing complex crystal structures\[9,10\] have been utilized.

For decades, nanoporous structure has been theoretically demonstrated effective in lowering thermal conductivity,\[11-13\] which should be a promising routine toward high-efficiency TE materials but has been more or less overlooked for a long time. Until recent years, increasing attention was paid on this strategy, for example, calculations by Prasher\[13\] had suggested that diffuse scattering at medium/pore interfaces would significantly reduce the thermal conductivity of the medium. Afterwards, Romano and Grossman\[14\] further identified the pore configuration that minimized thermal transport. Experimentally, by introducing hollow structures, Wu and co-workers successfully reduced the thermal conductivity of Bi\(_2\)Te\(_3\) to a low value of 0.5 W m\(^{-1}\) K\(^{-1}\).\[15\] Compared with the well-established nanostructuring techniques, such as introducing nano-inclusions/precipitates\[16-19\] or forming nanocomposites\[8\] with embedded nanoparticles, nanoporous structuring has the following advantages. First, nanopores have no influences on the chemical compositions of the matrix material. Second, nanopores are likely more stable at high temperatures than the precipitates that are usually formed by annealing. In addition, increasing pores can reduce the use of TE materials. However, related studies to date were limited to a few TE material systems,\[16-20\] such as SiGe-based alloys,\[16\] bismuth tellurides\[17\] and some oxides.\[18,19\] In the past decade, more studies have been devoted to searching for new TE materials and their chemical modifications for TE performance enhancement, while less attention has been paid to the importance of nanoporous structures. Only a few methods were reported on engineering the thermal transport of TE materials by introducing nanoporous structures, such as altering the sintering processes,\[17\] employing pore-forming agents,\[21\] or using wet-chemical synthesis to prepare hollow structured precursors.\[15,18\] This may also be due to the lack of techniques in precisely controlling the pore size, alignment, and configuration, etc.

In this paper, we reported a systematic study on nanoporous PbSe–SiO\(_2\) TE composites, in which nanosized SiO\(_2\) particles were used to create randomly distributed nanopores via a facile milling processing (mechanical alloying, MA), leading to greatly reduced thermal conductivity. In addition, the electrical transport was found to be governed by the grain-boundary potential barrier scattering (for simplicity, using “boundary-barrier scattering” instead in the following text) that is related to the incorporation of SiO\(_2\) nanoparticles and the presence of nanopores. A considerable \(ZT\) enhancement was achieved at high temperatures with the maximum value being 1.15 at 823 K, indicating the effectiveness of nanoporous structuring as a promising technique towards high TE performance.

Nanoporous PbSe–SiO\(_2\) Thermoelectric Composites

Chao-Feng Wu, Tian-Ran Wei, Fu-Hua Sun, and Jing-Feng Li*
2. Results and Discussion

X-ray diffractions revealed no significant differences among the compositions of PbSe + x vol% SiO2, indicating no other than the PbSe matrix with Fm3m symmetry, as depicted in Figure S1 (Supporting Information). In addition, no peaks related to oxides (either SiO2 or PbO) were observed but some traces of Pb peaks that appeared at around 32° (2θ) due to excessive Pb added. Accordingly, added SiO2 seemingly exhibits good chemical inertness during the fabrication process, which should benefit the electrical performances of these composites.

Figure 1 shows the micromorphologies of PbSe–SiO2 composites on fractured surfaces. At first sight, an obvious decrease in grain size was easily noticed with increasing SiO2 addition, that is, samples containing small amount (e.g., 0.1 vol%) of SiO2 were characterized with larger grains of 1–2 µm. On the contrast, for SiO2-rich compositions like the 0.9 vol% one, most grains were refined to smaller dimensions ≈400 nm, suggesting a successful suppression on grain growth by adding nano-SiO2 particles. Besides, compositing with SiO2 also brought about a remarkable increase in the porosity ($\phi = 1 - \rho / \rho_0$, where $\rho$ and $\rho_0$ are the measured and theoretical densities) of almost all compositions, as listed in Figure 1d. For $x = 0.9$, a large porosity of 14% was found accompanied with prevalent nanopores throughout the matrix as depicted in Figure 1c and Figure 2.

The nanopores are speculated to be induced by the SiO2 nanoparticles, probably ascribed to the good hydrophilicity[22] and abundant surfaces of nano-SiO2 particles, where the absorbed hydroxyl compounds (water and ethanol from wet-milling procedure) are vaporized during the sintering process and thus leave nanopores behind, as proposed in Figure 2. Intuitively, both refined grains and increased nanoporosity should be beneficial for scattering phonons with low-to-mEDIATE frequencies so as to limit the lattice thermal conductivity, which will be shown later.

All compositions exhibited typically degenerate behaviors, as the Seebeck coefficients increased linearly against temperature as shown in Figure 3. Since a similar doping level (0.2 mol% Cl) was intentionally controlled, different samples exhibited quite close thermopower values especially at elevated temperatures, although being slightly larger than that of the SiO2-free one probably due to additional scattering and lower carrier concentration as shown latter in Figure 3d. Indeed, at lower temperatures, the carrier transport seems more sensitive to other scattering centers apart from the acoustic phonons, for example, grain boundaries and nanopores, which leads to appreciable deviation from the common negative correlation between Seebeck coefficients and carrier concentration.[23]

Despite the small differences in thermopower, the electrical conductivity varied a lot among different compositions. An obvious decrease in electrical conductivity was observed with increasing SiO2 content in Figure 3c. Particularly, for samples with SiO2 contents over 0.5 vol%, especially the 0.9 vol% one, the electrical conductivity deviated from the normally decreasing tendency near room-temperature (RT), showing a “bump” between 323 and 523 K. Such an “abnormal” trend is ascribed to additional scattering processes, probably by grain boundaries or nanopores that involve energy barriers and exhibit different temperature dependence from the dominant acoustic phonon scattering. Nevertheless, as the temperature increases, free carriers become more energetic so that they experience less impact from energy-independent scattering centers like nanopores, causing limited damages to the high-temperature TE performances.

Figure 3d shows Hall carrier concentration and mobility at 323 K as functions of SiO2 volume fraction, where all SiO2-containing compositions exhibited similar $n_{hi}$ levels, but smaller than that of the SiO2-free one, which is probably ascribed to the element Cl loss during the synthesis with the existence of SiO2 particles. Besides, carriers from different samples distinguished themselves from others by the quite different mobility ($\mu_{hi}$) values. As can be seen, the $\mu_{hi}$ values were less changed with only 0.1 vol% SiO2 loaded, persisting $\approx 350$ cm2 V−1 s−1 but straightly downward to $\approx 200$ cm2 V−1 s−1 when the SiO2 content was up to 0.9 vol%.

Such a drop of mobility could be naturally ascribed to the incorporated SiO2 nanoparticles and resultant nanoporous structures, that is, nanoparticle scattering, nanopore scattering, composite effect, SiO2/matrix and pore/matrix interface scattering. Actually, nanoparticle scattering (as well as nanopore scattering) can be easily estimated by a typical nanoparticle scattering model[24]

$$\mu_{np} = \frac{eV}{\sigma_v v_e m_i}$$  (1)

where $V$ is the average volume of an individual nanoparticle/nanopore, $\sigma_v$ the scattering cross-section and $v_e$ the electron velocity. As calculated in Figure 4c, the contributions from these parts ($\mu_{np\text{particle}}$ and $\mu_{np\text{pore}}$) are relatively small, indicating that secondary SiO2 particles themselves, as well as nanopores, seemingly play a minor role here in scattering electrons
mainly due to their small amounts (corresponding to a bigger "V").

In addition, the large porosity can generate more immediate impacts upon the carriers, namely the composite effect, as seen from the similar dependence of $\phi$ and $\mu$ on $x$ (Figures 1d and 3d), which can be easily quantified by the effective medium theories.[25] Moreover, interface scattering (including particle/matrix and pore/matrix interfaces) is hard to be solely estimated here, for which it is taken as a part of another scattering mechanism discussed latter. At present, only the composite effect from the large porosity seems to account for the impaired mobility, however, as seen in Figure 4a, the temperature dependence of mobility is quite different for various compositions, indicating additional scattering mechanisms that cannot be simply ascribed to the composite effect. Indeed, polar optical scattering$^{[26,27]} (\mu_{po} \approx T^{-0.5})$ should be partly responsible for the deviation from acoustic domination ($\mu_{ac} \approx T^{-2.5}$ for PbSe) here, but cannot explain the ascent in $\mu$ for $x > 0.5$. Instead, ionized impurity scattering, from which carriers experience scatterings with even a positive temperature dependence of $\mu_{ii} \approx T^{1.5}$, however, should also be excluded due to the large static dielectric constants for lead chalcogenides and the low impurity levels$^{[27]}$ present in this work.

Instead, considering the nonexponential variation of $\mu$ and the presence of nanoporous structures, an additional scattering from boundary barriers is supposed to conform here, as previously observed in a variety of TE materials, for example, PbTe composites$^{[28]}$ and SnSe polycrystals$^{[29,30]}$. The boundary-barrier scattering is considered as the carrier trapping at grain boundaries with thermally activated dynamics. The effective mobility under boundary-barrier scattering is given by$^{[31]}

$$\mu_B = \frac{Lq}{(2\pi m^*k_BT)^{1/2}} e^{-\frac{E_b}{k_BT}}$$

(2)

where $L$ is the effective grain size, $q$ is the carrier charge, and $E_B$ is the height of energy barrier in the depletion region. At lower temperatures, individual discrepancy in electron transport is observed especially for the 0.7 and 0.9 vol% samples, which is regarded as an effect from boundary-barrier scattering induced by SiO$_2$ addition. Figure 4b displays the scattering mechanism analysis upon the boundary-barrier scattering model expressed as Equation (2). A good linearity of $\ln(\mu/T^{1/2})$ against $1/T$ is obtained for each composition, with roughly estimated energy barriers ($E_B$) of 32, 16, and 2.6 meV for the 0.9, 0.5, and 0.1 vol% samples respectively. The good linearity between these data further validates the existence of boundary-barrier scattering in such PbSe–SiO$_2$ composites.

Moreover, these energy barriers are believed to be generated by combined effects from refined grains and abundant nanopores generated by SiO$_2$ incorporation, including the interface scattering from particle/matrix and pore/matrix interfaces.

**Figure 2.** TEM morphologies for a) SiO$_2$ particles, b) nanoporous structure of the 0.9 vol% sample, c,d) residual SiO$_2$ particles around nanopores. e) A hypothesis for the formation of nanoporous structures in PbSe–SiO$_2$ composites according to the TEM observations.
In fact, by a repeated MA-SPS processing for the as-sintered 0.9 vol% sample, the porous structure vanishes (Figure S4, Supporting Information) with the mass density increased to over 95%. In this procedure, the as-sintered bulks were crushed and pulverized to powders again, which were subjected to secondary SPS. Different from the first one, there were less hydroxyl compounds absorbed to the SiO2 particles now, so less pores were created in the second sintering processing. As a result, the electrical performance was improved with decreased porosity as shown in Table 1 below, indicating the important role of nanopores instead of SiO2 themselves in dominating the electrical transport.

Taking into account the composite effect, boundary-barrier scattering and predominant acoustic phonon scattering (including polar optical scattering here), a good fitting between the mobility and SiO2 content is obtained as shown in Figure 4c, and these mobility components are also individually plotted, where the contribution from composite effect has been excluded beforehand. As is depicted, both scatterings from SiO2 particles and nanopores are negligible if compared with other mechanisms, such as acoustic phonons and boundary barriers, as we discussed above. Calculation details for mobility can be found in Supporting Information.

In addition, the boundary barrier is known as a thermally activated defect characterized with energy $E_b$, so its influence is fading away with increasing temperature. Others, such as the composite effect, would retain its influence but with a smaller contribution (to the total mobility values) because of enhanced acoustic phonon scattering at higher temperatures. As shown in Figure 4a, the mobility (above 700 K) differentiates less at high temperatures among samples with a slight decrease upon increasing SiO2 content and obeyed typical $T^{-2.5}$ law for lead chalcogenides,[27] suggesting the dominant role of acoustic phonon scattering on carriers. Thanks to limited influence from boundary-barrier scattering, the high-temperature electrical performance was less impaired by the SiO2 addition, providing certain possibility toward higher TE efficiencies.

Apart from the impaired carrier mobility, phonons in PbSe matrix also experiences intensified scattering over a wide temperature range. Figure 5 shows the total ($\kappa$) and lattice ($\kappa_L$) thermal conductivity values, where a declining tendency in both parameters was observed with increasing SiO2 content. Herein $\kappa_L$ is roughly calculated by extracting the electronic part according to $\kappa_e = \rho \sigma T$ under the assumption of acoustic-phonon scattering. Around RT, the $\kappa_L$ decreases from 1.6 W m$^{-1}$ K$^{-1}$ to an average value of 1.3 W m$^{-1}$ K$^{-1}$ as SiO2 was incorporated. As temperature increases, $\kappa_L$ decreases very quickly, downward to a plateau around 0.6 W m$^{-1}$ K$^{-1}$ before 600 K for most SiO2-contained samples, which is much smaller than the average $\kappa_L$ value of 0.8 W m$^{-1}$ K$^{-1}$ at 700–800 K for PbSe bulks.[10,31] The sharp decrease and the lower $\kappa_L$ values are considered associated with the SiO2 addition, probably with multiple effects from the abundant nanopores, interfaces, refined grains and SiO2 nanoparticles.

As is known, at high temperatures phonons are more energetic with higher frequencies and smaller MFPs (several
scattering at higher temperatures, which is similar with the nanoparticle scattering. \[26\] Additionally, for nanoporous structures, the existence of diffuse scattering\[13\] from medium/pore boundaries would further contribute to the phonon scattering due to the surface roughness, which enlarges the potential of nanopores on reducing $\kappa_L$ over a wider temperature region.

In order to assess the $\kappa_L$ reduction via various scattering processes, we compared the variation of $\kappa_L$ with both SiO$_2$ content and porosity, and more close correlations are found between the $\kappa_L$ reduction and the porosity, rather than the SiO$_2$ content. Figure 5b displays the $\kappa_L$ values as a function of SiO$_2$ content at 773 K, where an obvious decrease is found with increasing SiO$_2$ content up to 0.7 vol%, with $\kappa_L$ values decreasing from 0.8 to 0.56 W m$^{-1}$ K$^{-1}$ almost linearly. Further addition of SiO$_2$ seemingly causes less depression on phonon transport as the $\kappa_L$ value does not decrease any more. The minimum $\kappa_L$ was achieved in the 0.7 vol% sample, which is 30% lower than the average bulk values of 0.8 W m$^{-1}$ K$^{-1}$ and quite close to the limit obtained in nanostructured PbSe materials. \[35\] This reveals great potential of nanoporous structuring as an effective approach for lowering lattice thermal conductivity. Besides, it should be mentioned that increasing porosity has another advantage of reducing the weight of the thermoelectric materials and hence the devices.\[15\]

As is stated before, the $\kappa_L$ reduction here can be originated from various scattering centers, for example, nanoporous structures, boundaries, interfaces, or even SiO$_2$ nanoparticles. The effective thermal conductivity of the nanoporous composites from the Maxwell–Garnett result is given by\[36\]

$$\kappa_\text{eff} = \kappa_m \left( 1 - \frac{1 - \phi}{1 + \phi} \right) \kappa_m$$

where $\kappa_\text{eff}$ is the effective conductivity of the nanoporous composites, $\phi$ is the porosity, and $\kappa_m$ is the effective conductivity of the host medium. By substituting Equation (3) to the lattice thermal conductivity values, the effects on reducing thermal conductivity by nanoporous structuring can be more comprehensively understood. As depicted in Figure 5b (the yellow column and the inset), it is seen that the large porosity contributes a major part in help reducing the $\kappa_L$, approximately 50% (0.13 of 0.24 W m$^{-1}$ K$^{-1}$) for the 0.7 vol% sample, which is 30% lower than the average bulk values of 0.8 W m$^{-1}$ K$^{-1}$ and quite close to the limit obtained in nanostructured PbSe materials.\[35\] This reveals great potential of nanoporous structuring as an effective approach for lowering lattice thermal conductivity. Besides, it should be mentioned that increasing porosity has another advantage of reducing the weight of the thermoelectric materials and hence the devices.\[15\]

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role here with an estimation (Figure S6, Supporting Information) of 15%–25% contribution to the $\kappa_L$ reduction ($0.04–0.06$ of $0.24$ W m$^{-1}$ K$^{-1}$), probably due to the small MFPs of PbSe and large nanopore sizes.$^{[12]}$

As a result of the much lowered $\kappa_L$ in nanoporous composites and less impaired electrical performance at high temperatures, a maximum $ZT$ of 1.15 at 823 K was obtained in the 0.7 vol% sample, being an over 20% enhancement from n-type PbSe with only Cl doped and nearly 40% from PbSe$_{1-x}$Cl$_x$ materials synthesized by melting techniques,$^{[37]}$ as shown in Figure 6. Noticeably, an obvious $ZT$ enhancement around 600 K was observed at the same time, originating from the sharp decrease in thermal conductivity and the broad plateau of $\kappa_L$ on the minimum level, contributing to the enhancement of average $ZT$ at mediate temperatures. Actually, the average $ZT$ between 523 and 823 K exceeds 20% improvement, increasing from 0.7 in the 0 vol% sample upwards to 0.9 in SiO$_2$-containing ones. These results suggested the feasibility and promise of nanoporous structuring as an effective method to modify transport properties and improve the performances of TE materials.

3. Conclusion

In summary, SiO$_2$ addition has created abundant nanopores in PbSe–SiO$_2$ composites by a facile powder-based process. The existence of nanopores was found to introduce boundary barriers and impair charge transport but mainly at lower temperatures. Meanwhile, the porous structure also introduced additional scattering on phonons, thus significantly reducing the lattice thermal conductivity over a wide temperature range, leading to a maximum $ZT$ of 1.15 in the composition of PbSe + 0.7 vol% SiO$_2$ and also a higher average $ZT$ at mediate temperatures. This work experimentally substantiated the great potential of nanoporous structuring as an effective approach toward high-efficiency thermoelectrics.

4. Experimental Section

Synthesis: Bulk samples were synthesized by combining mechanical alloying (MA) and spark plasma sintering (SPS) using elemental Pb shots (99.999%, 1–3 mm), Se powders (99.99%, $\approx$ 75 µm), PbCl$_2$ (99.9%, $\approx$ 75 µm) and nanosized SiO$_2$ (99%, $\approx$ 10 nm) in the compositions of PbSe$_{0.998}$Cl$_{0.002}$ + $x$ vol% SiO$_2$ ($x = 0, 0.1, 0.3, 0.5, 0.7, 0.9$). The mixture of these powders was subjected to high-energy ball milling within a stainless steel vessel filled with protective Argon gas. After milling at 450 rpm for 24 h, the MAed powders were washed down by a wet-milling process using absolute ethanol for another hour. Afterward, the derived powders were vacuum-dried at 310 K and then sintered into plates by SPS (SPS211Lx, Fuji Electronic, Japan) at 873 K for 5 min under an axial pressure of 50 MPa.

Microscopic Identification: The phase structure and microstructure of sintered samples were investigated by X-ray diffractions using Cu-K$_\alpha$ radiation (XRD, D8 Advance A25, Bruker, Germany), field emission scanning electron microscopy (FESEM, Merlin VP compact, Zeiss, Germany) and transmission electron microscopy (TEM, 2100, JEOL, Japan), respectively. The elemental distribution was also validated

Figure 5. a) Total and lattice thermal conductivity values as a function of temperature, where the dashed gray line represents data of PbSe$_{0.998}$Cl$_{0.002}$ from our previous work. b) The $\kappa_L$ reduction evaluation for nanoporous PbSe–SiO$_2$ composites at 773 K, where the inset pie chart reveals the individual contribution of various scattering centers (including the pore composite effect, grain boundary and nanoparticles, and diffuse scattering) in reducing $\kappa_L$ for the 0.7 vol% composition.

Figure 6. ZT values of PbSe + $x$ vol% SiO$_2$ samples in this work, with previous results on Cl-doped PbSe as references.
using electron probe microanalysis (EPMA, JXA-8230, JEOL, Japan) on polished samples.

**Thermoelectric Measurement:** The Seebeck coefficient and electrical conductivity were measured by a Seebeck coefficient/electrical resistivity measuring system (ZEM-2, Ulvac-Riko, Japan) using bar samples, meanwhile, disk samples were machined for the thermal diffusivity (λ) measurements through the laser flash technique (TC9000, Ulvac-Riko, Japan), where the thermal conductivity was derived from the formula $\kappa = \Delta C_p d$, in which $C_p$ is the heat capacity determined by the composite effect of PbSe and SiO$_2$, and $d$ is the mass density obtained by the Archimedes method. To identify electrical transport mechanisms, Hall measurements were conducted through the Van der Pauw technique under a reversible magnetic field of 0.52 T (8340DC, Toyo, Japan). The uncertainty of each parameter is estimated to be about 4%, which combined leads to an uncertainty of ≈15% in ZT.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

mechanical alloying, nanoporous structures, thermoelectric composites

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