Supporting Information

Ultra-low thermal conductivity in B$_2$O$_3$ composited SiGe bulk with enhanced thermoelectric performance at medium temperature region

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1. The Lorentz calculation

Because the charge carriers transport both heat and charge, $\kappa_e$ is commonly estimated using the measured $\sigma$ by the Wiedemann-Franz law: $\kappa_e=L\sigma T$, where $L$ is the Lorenz number. Once $\kappa_e$ is known, $\kappa_l$ is computed by subtracting the $\kappa_e$ from the total thermal conductivity, $\kappa=\kappa_e+\kappa_l$.

For a single parabolic band, $L$ and $S$ are both functions of reduced chemical potential ($\eta$) and carrier scattering factor ($\lambda$) only, the value of $L$ is calculated according to the following formula:

$$L = \left(\frac{k_B}{e}\right)^2 \frac{(1 + \lambda)(3 + \lambda) F_{\lambda}(\eta) F_{\lambda+2}(\eta) - (2 + \lambda)^2 F_{\lambda+1}(\eta)^2}{(1 + \lambda)^2 F_{\lambda}(\eta)^2}$$

$$S = \frac{k_B}{e} \left(\frac{(2 + \lambda) F_{\lambda+1}(\eta)}{(1 + \lambda) F_{\lambda}(\eta)} - \eta\right)$$

Where $F_j(\eta)$ represents the Fermi integral,

$$F_j(\eta) = \int_0^\infty \frac{e^j d\epsilon}{1 + \exp[\epsilon - \eta]}$$

The Lorentz calculation values of different B$_2$O$_3$ adding amounts are shown in Fig. S1.

![Fig. S1 Lorentz calculated value.](image)
2. Effect of $\text{B}_2\text{O}_3$ on crystallization

In the main text, it can be seen from XRD pattern, the stronger peaks intensities with the increase of the $\text{B}_2\text{O}_3$ content indicate that adding of $\text{B}_2\text{O}_3$ promotes the crystallization of SiGe. In addition to XRD characterization, we prepared samples without and added with $\text{B}_2\text{O}_3$ with the same sintering method and sintering time, and then characterized by SEM. As shown in Fig. S1(a), many holes and poor compactness in the sample without $\text{B}_2\text{O}_3$ are disclosed under the premise of the same preparation process. Figure S1(b) shows the sample added with $\text{B}_2\text{O}_3$, which has good porosity and compactness, further illustrating that $\text{B}_2\text{O}_3$ can promote crystallization.

Fig. S2 (a) The SEM images of the sample without $\text{B}_2\text{O}_3$, (b) the SEM images of the sample added with $\text{B}_2\text{O}_3$

3. The EPMA measurement

EPMA works by bombarding micro-volume samples with focused electron beams and collecting X-rays emitted by various elements. Since the wavelengths of X-rays are characteristic of the emitting material, the sample components can be easily identified by recording wavelength dispersion spectra.

Figure. S3 is the EPMA test of $\text{Si}_{80}\text{Ge}_{20}\text{B}_{1.5}(\text{B}_2\text{O}_3)_{0.6}$ sample. It can be seen from the figure that the composition of point 1 and point 2 is different, and it can be judged that there are two phases. In addition, the sample was tested by surface scanning, and it was found that B element was distributed sporadically. It was inferred that it was probably a nano-second-phase containing $\text{B}_2\text{O}_3$, which needed to be further confirmed by TEM analysis.
4. The TEM observation

We have carried out TEM analysis in other different areas, and we can also find micropores, nano-second-phase, it is proved from the side that the micropores and the nano-second-phase are uniformly distributed.
5. Fitting calculation of lattice thermal conductivity

We use the Callaway model to calculate the lattice thermal conductivity,\(^1\)\(^-\)\(^^3\) and the details are as follows.

\[
k_l = \frac{k_B}{2\pi^2\nu} \int_0^{\theta_D/T} \frac{x^4e^x}{\tau_c^{-1}(e^x-1)^2} \frac{d\tau}{x}
\]

where \(x = \frac{\hbar\omega}{k_BT}\), \(k_B\), \(\omega\), \(\hbar\), \(\theta_D\), \(\nu\) and \(\tau_c\) are the reduced phonon frequency, Boltzmann constant, phonon frequency, reduced Planck constant, Debye temperature, sound velocity and phonon-scattering relaxation time, respectively.

The relaxation time is affected by point defect scattering, phonon-phonon scattering, stacking fault and electron-phonon scattering, second phase, micropore and grain boundary scattering, as shown in the following formula.

\[
\tau_c^{-1} = A\omega^4 + B\omega^2T\exp\left(-\frac{\theta_D}{3T}\right) + C\omega^2 + \frac{\nu}{d}
\]

Among them, \(A\omega^4\) corresponds to the relaxation time of the scattering of point defects, relaxation time of phonon-phonon scattering corresponding to \(B\omega^2T\exp\left(-\frac{\theta_D}{3T}\right)\), \(C\omega^2\) corresponds to the relaxation time of the stacking fault and electron-phonon scattering, \(\frac{\nu}{d}\) corresponds to the relaxation time of the second phase, micropore and grain boundary scattering.

Combined with the actual test results and literature values,\(^4\)\(^-\)\(^^8\) we get the parameters of the following table. The \(d\) is obtained from the grain size distribution and micropore size distribution of TEM images, and the \(B\) is obtained by fitting with \(k_l\) known in previous studies. The point defect scattering is not considered, but only phonon-phonon scattering, electron-phonon scattering and boundary scattering are considered, by fitting the experimental \(k_l\), \(C\) can be obtained when \(B\) is determined. On the premise that both \(B\), \(C\) and \(d\) are determined, combined with the actual test results, \(A\) is calculated.

<table>
<thead>
<tr>
<th>Composition</th>
<th>(A) (s(^^3))</th>
<th>(B) (s/K)</th>
<th>(C) (s)</th>
<th>(\frac{\nu}{d}) (s(^{-1}))</th>
</tr>
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<tbody>
<tr>
<td>Si(<em>{80})Ge(</em>{20})B(_{1.5}) (B(_2)O(_3)) 0.6</td>
<td>(3500 \times 10^{-45})</td>
<td>(37 \times 10^{-20})</td>
<td>(0.4 \times 10^{-17})</td>
<td>(8 \times 10^9)</td>
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Si$_{80}$Ge$_{20}$B$_{1.5}$

1400 $\times$ 10$^{-45}$  $37 \times 10^{-20}$  $8 \times 10^{-17}$  $2 \times 10^9$

References