Si$_2$Ge: A New VII-Type Clathrate with Ultralow Thermal Conductivity and High Thermoelectric Property

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Based on global particle-swarm optimization algorithm and density functional theory methods, we predicted an alloyed Si$_2$Ge compound with body centered tetragonal type VII clathrate (space group $I4/mmm$) built by a truncated octahedron fromed by six quadrangles and eight hexagons ($[4668]$). Si$_2$Ge clathrate is 0.06 eV/atom lower than VII Si clathrate and thermally stable up to 1000 K. It has an indirect band gap of 0.23 eV, high p-doping Seebeck coefficient and n-doping electrical conductivity. It owns a low lattice thermal conductivity of 0.28 W/mK at 300 K because of its weak bonding and strong anharmonic interaction of longitudinal acoustic and low-lying optical phonons. The moderate electronic transport properties together with low lattice thermal conductivity results in a high optimal thermoelectric performance value of 2.54 (1.49) at 800 (1000) K in n (p)-doped Si$_2$Ge.

Thermoelectric (TE) materials can realize the mutual conversion between heat and electricity, the search and preparation of high-performance TE materials have been received a great deal of attention from environment and energy communities. The efficiency is generally expressed as a dimensionless TE figure-of-merit (ZT). High ZT value depends on high Seebeck coefficient ($S$), high electronic conductivity ($\sigma$) and low thermal conductivity ($\kappa$) including electronic ($\kappa_e$) and lattice contributions ($\kappa_L$). These parameters are coupled with each other, so it is difficult to regulate independently and then improve TE performance. The ideal TE materials possess the structure only suppresses the movement of phonon and not the electrons. These materials are called as phonon glass electron crystal, or PGEC for short. Clathrates are one of PGEC materials and are considered as a newly classes of potential TE materials.

Inorganic clathrates are those “open-structured” compounds consisting of 3D network framework mostly formed by group 14 atoms (Si, Ge or Sn) through covalent tetrahedral bonds, creating cavities or cages in which metal atoms are embedded. The clathrates have been gain more interesting because of their transport properties and wide band-gap range show promising TE and optical application. Although the clathrates have so many advantages, their ZT is below 0.2 for Si-based due to their poor power factor. SiGe alloyed clathrates exhibit a significant increase in TE performance from their high power factor ($P_F$, $S^2\sigma$) and low lattice thermal conductivity. Apart from this, SiGe alloyed clathrates have a great potential in terms of superior optical and electrical properties. This phenomenon does not only exist in the clathrates, many researches reveal that alloyed inducing band convergence is responsible for the high Seebeck coefficients and tuning the electrical properties as result of modifying the band structure, and thus leading to a significant increase of TE performance in alloy compounds. Therefore, a clathrate containing both Si and Ge atoms with moderate electron and phonon transport will be of great TE performance.

Herein we report a new Si$_2$Ge-clathrate compound with the sodalite-type structure using global particle-swarm optimization algorithm and density functional theory. This clathrate is made up of a (Si$_8$Ge$_4$)$_2$ tetrakaidecahedra, which could be extending in a $2 \times 2 \times 2$ supercell with a structure like conventional sodalite. It has a 0.23 eV indirect band gap. Such a Si$_2$Ge clathrate is 0.06 eV/atom lower than the Si-VII type clathrate, and holding the cage configuration up to 1000 K. Si$_2$Ge is essentially guest-free and possesses a very low thermal conductivity of 0.28 W/mK at 300 K because of the strong coupling between longitudinal acoustic (LA) and low-lying optical (LLO) phonons. This coupling reveals an avoided-crossing behaviour of LA and LLO originates from...
an anharmonic interaction. Furthermore, the calculated Seebeck coefficient and electronic conductivity suggest desirable TE properties in this Si2Ge clathrate. The optimized ZT value is about 2.54 and 1.49 for n- and p-doping Si2Ge clathrate.

Methods

Structure prediction. We employ the efficient particle swarm optimization (CALYPSO) code24 to search for low-energy 3D Si2Ge clathrate. The number of formula units per simulation cell is set to be 1−2. Unit cells containing total number atoms of 6 and 12 are considered. The structure relaxations are performed using Vienna ab initio simulation package (VASP)25,26. The projector-augmented plane wave (PAW) approach27 is used to represent the ion-electron interaction. The generalized gradient approximation in the form of Perdew, Burke and Ernzerhof (PBE) is adopted28. The plane-wave cutoff energy for wave function is set to 600 eV. Monkhorst-Pack k-mesh of 5 × 5 × 5 is adopted to represent the first Brillouin zone. For structure optimization, the convergence thresholds are set to 10−7 eV and 10−3 eV/Å for total energy and force component, respectively.

Electronic and phonon structure. The Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional29,30 are also used for the high accuracy of electronic structure calculations. The plane-wave cutoff energy for wave function is set to 400 eV. Monkhorst-Pack k-mesh of 7 × 7 × 7 is adopted to represent the first Brillouin zone. Ab initio molecular dynamics (AIMD) simulations at different temperatures are performed using the canonical ensemble (NVT) with the Nosé thermostat31 to examine thermal stability. Simulations lasted for 10 ps with a time step of 1 fs at the temperature of 500, 1000, and 1200 K were carried out. Phonon spectrum calculation is carried out using the linear response method within density functional perturbation theory32 implemented in the Phonopy package33.

TE performance calculation. Based on the Boltzmann transport theory, the Seebeck coefficient, the ratio of electrical conductivity to electrical relaxation time and the electronic thermal conductivity are evaluated by using the semiclassical Boltzmann transport theory with the relaxation time approximation, which is implemented in the so-called BoltzTraP code34. Here it is assumed that the acoustic phonon is the main scattering mechanism, we calculated carrier mobility by the deformation potential (DP) theory35 as following36,37

\[
\mu = \frac{\tau e}{m^*} = \frac{3}{2\pi^2}\frac{h^4}{\rho^2}\frac{\mu^* e^2}{3m^2(k_BT)^{3/2}E^2}
\]  

where \( \mu \) is carrier mobility, \( m^* \) is inertial effective mass, \( \rho \) is the density of states effective mass of a single band, \( \mu \) is the crystal mass density, \( v \) is the average sound velocity from phonon dispersion listed in Table S1 (Supplementary Information). The term \( E \) represents the deformation potential constant of the valence-band minimum (VBM) for hole or conduction-band maximum (CBM) for electron along the transport direction. The deformation potential constant (\( E_j \)) is calculated by the linear fitting of the CBM (VBM)–strain relation, the result is shown in Fig. S1 (Supplementary Information). With \( E_j \) and the effective mass is known, the carrier motilities are calculated by Eq. (1).

Lattice thermal conductivity. The first-principles lattice thermal conductivity \( \kappa \) was calculated by solving Boltzmann transport equation for phonons. The interatomic force constants (IFCs) were calculated within a real-space supercell approach using the Phonopy package33 for the two-order harmonic IFCs and the ShengBTE package38 for the third-order anharmonic IFCs. The IFCs were calculated using a 3 × 3 × 3 supercell with a 19 × 19 × 19 q-mesh. The electron-phonon (e-p) coupling properties are obtained using the Quantum Espresso package39 with ultrasoft pseudopotentials, energy cutoff of 40 Ry and a q-grid of 8 × 8 × 8.

Results and Discussion

The stable structure of Si2Ge obtained from global structure search is shown in Fig. 1. The optimized Si2Ge crystallizes in the Tetragonal space group, I4/mmm (no. 139), with a = b = 6.759 Å, c = 6.868 Å (Fig. 1). The lattice strain is mostly induced by the distorted tetrahedral coordination of SiGe alloy, or, alternatively, by the 90.2° (\( \angle \text{SiGeSi} \)) and 89.7° (\( \angle \text{SiGeSi} \)) of 4-membered (Si2Ge2) rings along c direction. The 3D framework is composed of a 24-atom tetrakaidecahedra (Si8Ge4)2 formed by four-fold coordination of Si at 8j and Ge at 4d sites (Fig. 1b,d). The clathrate-forming polyhedron is a truncated octahedron, so-called clathrate-VII pattern40, formed by six quadrangles and eight hexagons (\([4^6]e\)) of 4-membered rings along c direction (Fig. 2). The Si and Ge-VII clathrate is 0.11 and 0.06 eV/atom lower in energy than Si-VII clathrate, but higher than those well-known Si-II and Si-VIII clathrates (0.10 and 0.07 eV/atom) because of containing a large number of four-membered rings resulting strained in comparison to type II frameworks41. The bond lengths in Si2Ge clathrate are 2.37 Å for Si-Si and 2.45 Å for Si-Ge, respectively. These values are slightly larger than 2.35 Å for diamond-Si, 2.38 Å (Si-Si) for Type-I Si clathrate42, 2.36–2.42 Å (Si-Ge) for Si14Ge14 alloy clathrate44. Generally, a longer bond length corresponds to weaker bond interaction, and weak bond interaction decrease the speed of the sound, which conversely drop the thermal conductivity of the lattice45. Therefore Si2Ge-VII clathrate shows relatively stable and weak covalent bonds which is responsible for the low lattice thermal conductivity.

Also, we simulate the thermal stability of Si2Ge clathrate. A 3 × 3 × 3 supercell is used in the simulations at temperatures of 500, 1000 and 1200 K by performing ab initio molecular dynamics (AIMD) simulations. The snapshots of the geometries at the end simulations show that Si2Ge clathrate can maintain its original configuration at temperature up to 1000 K (Fig. 2). At 1200 K, some bonds begin to break and lead to cage structure distorted. The radical distribution functions (RDF, Fig. S2, Supplementary Information) at 500 K and 1000 K have also shown the typical feature of VII-type clathrate. When the temperature reaches 1200 K, RDF exhibit a few feature of liquid. This indicates that Si2Ge has a melting/decomposition temperature close to that of Si and Ge-based clathrates. For instance, Ba4Al13Si11 melts at 1073 K44, and Sr5Ga14Ge10 melts congruently at 1033 K45.
The well-preserved geometry of Si\(_2\)Ge at such high temperature suggests the thermal stability of Si\(_2\)Ge clathrate and its possible utilization at a high temperature.

Figure 3a and Table 1 show the band structure, effective mass and carrier mobility for Si\(_2\)Ge. It is shown that an indirect band gap of 0.23 eV for Si\(_2\)Ge from Fig. 3a. The valence band maximum (VBM) is located at the Z point with 3-degeneracy, are named by VB1, VB2 and VB3 in Fig. 3a. The conduction band minimum (CBM) is along the Z-\(\Gamma\) line of 2-degeneracy imposed by the symmetry of the Brillouin zone which is shown in the inset of Fig. 3a. It is obvious that p-type doped will display slightly higher degeneracy of carrier pockets than that of n-type doped Si\(_2\)Ge. It is well known the Seebeck coefficient is proportional to the density of state effective mass\(^2,4,6,22\), given by

\[
m_{d}^{*} = \frac{N_{v}}{2^{1/3} m_{s}}
\]

where \(N_{v}\) represent the number of degenerate. \(m_{s}\) can be obtained by

\[
m_{s} = \left(\frac{1}{m_{1}^{-1} + \frac{1}{m_{2}^{-1}} + \frac{1}{m_{3}^{-1}}}\right)^{1/3}.
\]

Accordingly, \(m_{d}^{*}\) of valence band is 1.30 and 0.64 \(m_{0}\) for VB1(2) and VB3 receptively, while 0.57 \(m_{0}\) of conduction band, indicating heavier hole mass behavior.

The optimal ZT performance is determined by the weighted mobility, ZT \(\propto\) \(\mu(m_{d}^{*}/m_{0})^{3/2}\) (refs. 3,4,6–49). Taking the assumption of acoustic or optical phonon scattering are predominant for charge carriers, the mobility can be expressed as \(\mu \propto 1/(m_{d}^{*}m_{i}^{*})\), as mentioned in (1). Additionally, the optimal ZT \(\propto N_{v}/m_{i}^{*}\), is inversely proportional to \(m_{i}^{*}\) (ref. 4). \(m_{i}^{*}\) can be calculated by

\[
m_{i}^{*} = \frac{3}{1/m_{1} + 1/m_{2} + 1/m_{3}}.
\]

The mobility of n-type Si\(_2\)Ge can be estimated to be 83 cm\(^2\)/Vs using the average \(m_{i}^{*} = 0.36\) \(m_{0}\) of conduction band. Then, we can estimate the constant carrier scattering time \(\tau = 47\) fs at 300 K for n-type Si\(_2\)Ge. Similarly, the hole mobility and its relaxation time are also listed in Table 1. Consequently, the multiple degenerate valence band (VB1 and VB2) producing a large \(m_{d}^{*}\) and thereby a high S with explicitly reduced the hole mobility. Compared with the valence band, the light \(m_{d}^{*}\) and

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**Figure 1.** (a) The unit cell structure of VII-type Si\(_2\)Ge clathrate marked by black lines (b,c) Linkage of tetrakaidecahedra along selected directions. (d) The 3D sodalite framework of Si\(_2\)Ge. Tetrakaidecahedron (Si\(_8\)Ge\(_4\))\(_2\): blue polyhedron, yellow apex: Si atom; green apex: Ge atom.

**Figure 2.** Snapshot of the Si\(_2\)Ge at 10 ps of the ab initio molecular dynamics simulation in the NVT ensemble. The optimized Si\(_2\)Ge was used as the initial structure. The temperature of the system was controlled at 500 K, 1000 K and 1200 K. The estimated melting temperature is around 1200 K. Yellow apex: Si atom; green apex: Ge atom. The dotted red lines represent the broken bonds.
Therefore, for Si$_2$Ge, deformation potential method can give a reasonable carrier relaxation time. The phonons in this region are mainly derived from the acoustic branches. The boundary frequency of LLO$_1$ branch at the $\Gamma$ point is lapped with the longitudinal acoustic (LA) phonons. The boundary frequency of LLO$_1$ branch at the $\Gamma$ point is about 1.2 THz (43 cm$^{-1}$) and is similar to most of the LLO phonons in other low $\kappa_L$ PGE compounds, for example, Yb filled skutterudites (42 cm$^{-1}$)$^{49}$ and Ba$_8$Ga$_{16}$Ge$_{30}$ (44 cm$^{-1}$)$^{52}$. LLO branches have such large phonon dispersion slope near the $\Gamma$ point, which means high phonon velocity and strong anharmonic behaviour and may be provided essential scattering channels for heat-carrying phonons, similar to that of PbTe$^{52-54}$. More importantly, the “avoided crossing” interaction between LLO and longitudinal acoustic (LA) branches has been observed in Fig. 4a along Z-$\Gamma$ line at 1.5 THz. There is a small gap at avoided crossing point indicates strength of coupling between LA and LLO modes seen from the inset of Fig. 4a. It leads to enhance the phonon scattering rates and reduce acoustic mode velocities, and then result the low $\kappa_L$.

Figure 4b shows the Grüneisen parameter ($\gamma$) for Si$_2$Ge as a function of the phonon frequency. The $\gamma$ shows similar features as the Si-VII$^{55}$, where negative $\gamma$ are spread out at low frequency values. TA and LLO branches possess high absolute $\gamma$, typically, the minimum $\gamma$ is extraordinarily low $\sim$–14.16. The average Grüneisen parameter calculated from ShengBTE is 3.19 at 300 K. This value is a little larger than that of AgSbSe$_2$ (3.05, a low thermal conductivity material, 0.48 W/mK at 300 K)$^{56}$. The acoustic and LLO modes have much larger absolute $\gamma$ and play an important role in lattice thermal resistance of Si$_2$Ge.

The phonon scattering rates (SC) related to phonon-phonon interactions (PPI) and electron-phonon (EPI) are shown in Fig. 5a. The phonon-phonon SC from acoustic phonons is as low as the order of 0.006 ps$^{-1}$, while the low lying optical phonons is in the range of 0.06–8 ps$^{-1}$ and are 1–2 orders of magnitude higher than acoustic branches with frequencies above ~5 THz for Si$_2$Ge clathrate. High SC around 5 THz from flat optical phonons.
One can see the electron-phonon SC due to EPI is much smaller than the phonon-phonon scattering. Si$_2$Ge has
stronger lattice anharmonicity, as a consequence, electron-phonon scattering nearly has no contributions to the
lattice thermal transport.

Based on ShengBTE, Si$_2$Ge actually possess a low lattice thermal conductivity seen from Fig. 5b. With the tem-
perature rising the lattice thermal conductivity decreases monotonically. At 300 K, lattice thermal conductivity
is 0.28 W/mK, which is lower than majority of clathrates, such as Sr$_8$Ga$_{16}$Ge$_{30}$ (0.9 W/mK)$^{45}$, Sn-based clathrates
(=1 W/mK)$^{57}$, and comparable to the unconventional transition metal-phosphorus clathrates with ordered super-
structures and heavy elements, such as Ba$_8$Cu$_{16}$P$_{30}$ (=0.3 W/mK)$^{58}$ and Ba$_8$Au$_{16}$P$_{30}$ (=0.2 W/mK)$^{59}$. At 1000 K the
lattice thermal conductivity decreases dramatically to ~0.12 W/mK, which is lower than that measured for SnSe
single crystals at 973 K (0.23 ± 0.03 W/mK)$^{60}$. The inset of Fig. 5b shows the cumulative lattice thermal conductiv-
ity vs. phonon frequnency of Si$_2$Ge. We found that the lattice thermal conductivity increases quickly with
$\omega$ in the low-frequency region. By setting a cutoff of 4 THz, the accumulated thermal conductivity is found to be as high as
~73%, which means low frequency (<4 THz) phonons may make an importance role on $\kappa_L$ due to low scattering
rates because of large group velocity of acoustic modes which are mainly from vibration of Ge discussed in the
previous description (see Fig. 3b). The high-frequency optical phonons have SC of 1 ps$^{-1}$, which are less contribu-
tion on heat current. The cumulative lattice thermal conductivity divided by total lattice thermal conductivity of
Si$_2$Ge with respect to phonon mean free path (MFP) at 300, 500 and 1000 K, are plotted in in Fig. 5c. As the MFP
increases, the normalized $\kappa_L$ integration increases, and then approaches 1. It is found that the thermal conductiv-
ities are dominated by phonons with MFPs ranging from 0.1 to 5 $\mu$m at room temperature. At width about 70 nm,
the lattice thermal conductivity drops about 50%. At high temperatures, the phonon MFPs become even shorter,
the MFP corresponding to the median $\kappa_L$ accumulation in Si$_2$Ge reduces from 33 nm at 500 K to 19 nm at 1000 K.
The phonon MFPs in Si$_2$Ge are notably longer than those in other clathrate (around 10 nm at 300 K for Type-I Si
clatrate$^{61-63}$, which means $\kappa_L$ of Si$_2$Ge is more sensitive to size effects.

The electronic thermal conductivity ($\kappa_e$) was evaluated via Wiedemann-Franz law: $\kappa_e = L_0 \sigma T$ with
$L_0 = 2.44 \times 10^{-8} \text{W} \cdot \text{K}^{-2}$, The Seebeck coefficient S, electrical conductivity $\sigma$, and TE power factor $S^2\sigma$ (PF) as
a function of carrier concentration at 300 K have been shown in Fig. 6. Clearly, p-doped Si$_2$Ge has the higher

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**Figure 4.** (a) Details of the low-energy (<4 THz) of the phonon spectrum of Si$_2$Ge along the Z–Γ, Γ–M, N–Γ
and Γ–Y directions. The green ellipse highlight avoided-crossing points between the acoustic and optical
modes. (b) Grüneisen parameter for Si$_2$Ge.

**Figure 5.** (a) Phonon–phonon scattering rates vs. frequency of acoustic (pink circles), low-lying optical (green
triangles), other optical (blue stars) phonons and electron-phonon interaction scattering rates (yellow circles) for
Si$_2$Ge calculated at 300 K. (b) Lattice thermal conductivity $\kappa_L$ as a function of temperature for Si$_2$Ge. The inset
shows accumulated lattice thermal conductivities with respect to frequency (black lines), and the derivatives
(red lines). (c) Normalized $\kappa_L$ integration for Si$_2$Ge with respect to the phonon MFP at 300, 500 and 1000 K.
Seebeck coefficient than n-dope ones over the full carrier concentration range (0.01–10 × 10²⁰ cm⁻³), while the higher conductivity values of electrons than that of holes. This consistent with the discussed above. Since $S$ decreases as carrier concentration where $\sigma$ increase, the maximum power factor is 0.63 mW/mK² at the hole concentration of 1.91 × 10²⁰ cm⁻³, while 2.81 mW/mK² at the electron concentration of 4.31 × 10¹⁹ cm⁻³. From Fig. 6c, at 300 K, the n-type power factor is much higher than p-type, which further confirmed that the low effective mass contributes to the enhancement of the TE performance.

ZT at different temperature vs. carrier concentration is plotted in Fig. S4 (see Supplementary Information). The ZT value is peaked at a specific carrier concentration at the different temperature. For electrons at room temperature, the peaked ZT value is predicted to be 0.41 at 5.41 × 10¹⁸ cm⁻³ and that for holes is 1.09 at 5.41 × 10¹⁸ cm⁻³. This peaked ZT value is named the maximum ZT ($ZT_{max}$). $ZT_{max}$ as a function of temperature is plotted in Fig. 7, which demonstrates a linear increase below 800 K and then decrease for n-doped, while a linear increase with temperature for p-doped. The highest $ZT_{max}$ achieved at 800 K is 2.54 for n-doped Si₂Ge clathrate and 1.49 for p-doped at 1000 K. These values are superior those realized in K₈Ba₁₆Ga₄₀Sn₉₆ (n-type, 1.12 at 637 K)⁶⁴, and type-I Ba₈Ga₁₆Ge₃₀ (p-type, 1.10 at 823 K)⁶⁵.

To summarize, we extend a new clathrate materials, namely Si₂Ge-VII clathrate on basis of global structure search and density functional theory. This clathrate has a tetrakaidecahedral lattice similar to sodalite and exhibits excellent thermal and dynamical stabilities. Si₂Ge clathrate has an indirect band gap of 0.23 eV, with higher p-doping Seebeck coefficient owing to higher hole density-of-sates mass and higher n-doping electrical conductivity thanks to lower electron effective mass. Interestingly, it owns a low lattice thermal conductivity due to its weak bonding interaction and strong anharmonic LA-LLO coupling results in avoided-crossing. The fascinating electronic properties together with the low lattice thermal conductivity make Si₂Ge clathrate a promising TE
material. We attribute the remarkably high ZT peak of Si2Ge (n-type 2.54 at 800 K and p-type 1.49 at 1000 K). This study would enrich the diversity and boost the development of TE materials.

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

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References
1. Kleinke, H. New bulk Materials for Thermoelectric power generation: clathrates and complex ammonides. *Chem. Mater.* **22**, 604–611 (2010).
2. Slack, G. A. *CRC Handbook of Thermoelectrics*, Vol. 407 (CRC Press, Boca Raton, 1993).
3. Nolas, G. S., *Thermoelectrics: basic principles and new materials developments*. G. S. Nolas, J. Sharp & H. J. Goldsmid. (Springer: Berlin, London, 2001).
4. Nolas, G. S., Slack, G. A. & Schujman, S. B. Chapter 6 semiconductor clathrates: a phonon glass electron crystal material with potential for thermoelectric applications. *Semiconduct. Semin.***69**, 255–300 (2001).
5. Nolas, G. S., Chakoumakos, B. C., Mahieu, B., Long, G. J. & Weakly, T. J. R. Structural characterisation and thermal conductivity of type-I tin clathrates. *Chem. Mater.* **12**, 1947–1953 (2000).
6. Karttunen, A. J., Fassler, T. E., Linnolahti, M. & Pakkanen, T. A. Structural principles of semiconducting group 14 clathrate frameworks. *Inorg. Chem.* **50**, 1733–1742 (2011).
7. Nolas, G. S., Cohn, J. L., Slack, G. A. & Schujman, S. B. Semiconductor Ge clathrates: promising candidates for thermoelectric applications. *Appl. Phys. Lett.* **73**, 178–180 (1998).
8. Cohn, J. L. et al. Glass-like heat conduction in high-mobility crystalline semiconductors. *Phys. Rev. Lett.* **82**, 779–782 (1998).
9. Adams, G. B. et al. Wide-band-gap Si in open fourfold-coordinated clathrate structures. *Phys. Rev. B* **49**(1994), 8048–8053 (1994).
10. Stefanosi, S., Malliakas, C. D., Kanatzidis, M. G. & Nolas, G. S. Synthesis and structural characterization of NaSi2S3 (0 < x < 24) single crystals and low-temperature transport of polycrystalline specimens. *Inorg. Chem.* **51**, 8686–8692 (2012).
11. Baran, V. et al. A combined metal-halide/metal flux synthetic route towards type-I clathrates: crystal structures and thermoelectric properties of AABnS3B8 (A = K, Rb, and Ca). *Chem. Eur. J.* **18**, 15077–15088 (2014).
12. Beekman, M. et al. Intrinsic electrical and thermal properties from single crystals of Na2Si136. *Phys. Rev. Lett.* **104**, 018301 (2010).
13. Leszczyński, J., Kolezyński, A. & Wojciechowski, K. T. Electronic and transport properties of polycrystalline Ba8Ga15Ge31 type I clathrate prepared by SPS method. *J. Solid State Chem.* **193**, 114–121 (2012).
14. Saiga, Y. et al. Optimization of thermoelectric properties of type-VIII Clathrate Ba4Ga32S40 by carrier tuning. *J. Alloy. Compound.* **507**, 1–5 (2010).
15. Cederkrantz, D., Saramat, A., Snyder, G. I. & Palmqvist, A. E. C. Thermal stability and thermoelectric properties of p-type Ba4Ga32S40 clathrates. *J. Appl. Phys.* **106**, 074509 (2009).
16. Martin, J., Nolas, G. S., Wang, H. & Yang, J. Thermoelectric properties of Silicon-Germanium type I clathrates. *J. Alloy. Compound.* **102**, 103719 (2017).
17. Baranowski, L. L. et al. Synthesis and optical band gaps of alloyed Si-Ge type II clathrates. *J. Mater. Chem. C* **2**, 3231–3237 (2014).
18. Moriguchi, K., Munetoh, S. & Shintani, A. First-principles study of Si34-xGex clathrates: direct wide-gap semiconductors in Si-Ge alloys. *Phys. Rev. B* **62**, 7138–7143 (2000).
19. Al Orabi, R. A. et al. Band degeneracy, low thermal conductivity, and high thermoelectric figure of merit in SnTe-CaTe alloys. *Chem. Mater.* **28**, 376–384 (2016).
20. Tan, G. et al. Valence band modification and high thermoelectric performance in SnTe heavily alloyed with MnTe. *J. Am. Chem. Soc.* **137**, 11507–11516 (2015).
21. Jiang, G. et al. High performance Mg2(Si,Sn) solid solutions: a point defect chemistry approach to enhancing thermoelectric properties. *Adv. Funct. Mater.* **24**, 3776–3781 (2014).
22. Zhao, L. D. et al. Thermoelectric and mechanical properties of nano-sic-dispersed Bi2Te3 fabricated by mechanical alloying and spark plasma sintering. *J. Alloy. Compound.* **455**, 259–264 (2008).
23. Li, W. et al. Band and scattering tuning for high performance thermoelectric Sn1-xMnxTe alloys. *J. Materiomic.* **1**, 307–315 (2015).
24. Wang, Y. C., Lv, J. A., Zhu, L. & Ma, Y. M. Crystal structure prediction via particle-swarm optimization. *Phys. Rev. B* **82**, 134106 (2010).
25. Savin, A., Nesper, R., Wengert, S. & Fassler, T. F. ELF: The electron localization function. *Chem.-Eur. J.* **6**, 3231–3237 (2010).
26. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15–50 (1996).
27. Bölö, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953–17997 (1994).
28. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
29. Heyd, J., Scuseria, G. E. & Ernzerhof, M. Erratum: Hybrid functionals based on a screened coulomb potential [J. Chem. Phys. 118, 8027 (2003)]. *J. Chem. Phys.* **124**, 219906 (2006).
30. Heyd, J., Scuseria, G. E. & Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. *J. Chem. Phys.* **118**, 8207–8215 (2003).
31. Nose, S. A Unified formulation of the constant temperature molecular-dynamics methods. *J. Chem. Phys.* **81**, 511–519 (1984).
32. Gonze, X. First-principles responses of solids to atomic displacements and homogeneous electric fields: Implementation of a conjugate-gradient algorithm. *Phys. Rev. B* **55**, 10337–10354 (1997).
33. Togo, A., Ōba, E. & Tanaka, I. First-principles calculations of the ferroelastic transition between rutile-type and CaO2-type SiO2 at high pressures. *Phys. Rev. B* **78**, 134106 (2008).
34. Madsen, G. K. H. & Singh, D. J. Boltztrap: A code for calculating band-structure dependent quantities. *Compu. Phys. Commun.* **175**, 67–71 (2006).
35. Bardeen, J. & Shockley, W. Deformation potentials and mobilities in non-polar crystals. *Phys. Rev. B* **80**, 72–80 (1950).
36. Goldsmid, H. J. *Thermoelectric Refrigeration*. (Plenum Press: New York, 1964).
37. Brooks, H. Theory of the electrical properties of germanium and silicon. *Adv. Electron. Electron. Phys.* **7**, 85–182 (1955).
38. Li, W., Carrete, J., Katcho, N. A. & Mingo, N. ShengBTE: A solver of the Boltzmann transport equation for phonons. *Compu. Phys. Commun.* **185**, 1747–1758 (2014).
39. Giannozzi, P. et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys.: Condens. Matter.* **21**, 395502 (2009).
40. Dolyniuk, J.-A., Owens-Baird, B., Wang, J., Zajkina, J. V. & Kovnir, K. Clathrate thermoelectrics. *Mat. Sci. Eng. R.* **108**, 1–46 (2016).
41. Kasper, J. S., Hagemuller, P., Pouchard, M. & Cros, C. Clathrate Structure of Silicon Na8Si46 and NaSi136 (x <1). *Science* **150**, 1713–1714 (1965).
64. Kishimoto, K., Koda, S., Akai, K. & Koyanagi, T. Thermoelectric properties of sintered type-II clathrates (K,Ba)24(Ga,Sn)136 with
66. A. Fonari, C. Sutton, Effective Mass Calculator, https://github.com/afonari/emc. (2012).
57. Nolas, G. S., Weakley, T. J. R. & Cohn, J. L. Structural, chemical, and transport properties of a new clathrate compound: Cs8Zn4Sn42.
58. Dolyniuk, J. A.
59. Fulmer, J.
60. Zhao, L. D.
61. Prabhjot, K., Georg, K. H. M. & Chandan., B. Thermoelectric Figure of Merit and Thermal Conductivity of Type-I Clathrate Alloy
56. Nielsen, M. D., Ozolins, V. & Heremans, J. P. Lone pair electrons minimize lattice thermal conductivity. Energ.
42. Wang, H., Chu, W., Hao, J. & Xiong, Y. Atomic simulation of Si–Ge clathrate alloys. Chem. Phys. 344, 299–308 (2008).
43. Zeier, W. G. et al. Thinking like a chemist: intuition in thermoelectric materials. Angew. Chem. Int. Edit. 55, 6826–6841 (2016).
44. Anno, H. & Shiratari, K. Thermal stability and oxidation resistance of polycrystalline Ba8Al16Si30-based clathrates. Phys. Status.
Solidi A 211, 1288–1292 (2014).
45. Schuiman, S. B. et al. Structural analysis of Sr8Ga16Ge30 clathrate compound. J. Alloy. Compound. 87, 1529–1533 (2000).
46. Pei, Y. et al. Convergence of electronic bands for high performance bulk thermoelectrics. Nature 473, 66–69 (2011).
47. Pei, Y., LaLonde, A. D., Wang, H. & Snyder, G. J. Low effective mass leading to high thermoelectric performance. Energ. Environ. Sci.
5, 7963–7969 (2012).
48. Chasmar, R. P. & Stratton, R. The thermoelectric figure of merit and its relation to thermoelectric generators. J. Electron. Contr. 7, 52–72 (1959).
50. Y ang, J. Thermoelectric properties of K8Sn30 and new types of clathrates. J. Physics. Cond. Matter. 7, 5675–5689 (1995).
51. Christensen, M. et al. Avoided crossing of rattler modes in thermoelectric materials. Nat. Mater. 7, 811–815 (2008).
52. Tian, Z. et al. Phonon conduction in PbTe, PbTe1-xSex from first–principles calculations. Phys. Rev. B 85, 184303 (2012).
53. An, J. M., Subedi, A. & Singh, D. J. Ab initio phonon dispersions for PbTe. Solid State Commun. 148, 417–419 (2008).
54. Delaire, O. et al. Giant anharmonic phonon scattering in PbTe. Nat. Mater. 10, 614–619 (2011).
55. Nolas, G. S., Weakley, T. J. R. & Cohn, J. L. Structural, chemical, and transport properties of a new clathrate compound: Cs8Zn4Sn42. Chem. Mater. 11, 2470–2473 (1999).
58. Dolyniuk, J. A. et al. Chemical bonding and transport properties in clathrates-I with Cu–Zn–P frameworks. Chem. Mater. 30, 3419–3428 (2018).
60. Zhao, L. D. et al. Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals. Nature 508, 373–377 (2014).
61. Prabhjot, K., Georg, K. H. M. & Chandan., B. Thermoelectric Figure of Merit and Thermal Conductivity of Type-I Clathrate Alloy Nanowires. RSC Advances. 9, 1–5 (2019).
62. Ohtaki, M. & Miyaishi, S. Extremely Low Thermal Conductivity in Oxides with Cage-Like Crystal. J. Electronic Mater. 42, 1299–1302 (2013).
63. Lory, P.-F. et al. Direct measurement of individual phonon lifetimes in the clathrate compound Ba7.81Ge40.67Au5.33. Nat. Commun. 8, 1–10 (2017).
64. Kishimoto, K., Akai, K. & Koyanagi, T. Thermoelectric properties of sintered type-II clathrates (K,Ba)24(Ga,Sn)136 with various carrier concentrations. J. Alloy. Compound. 118, 125103 (2015).
65. Wang, L.-H. & Chang, L.-S. Thermoelectric properties of p-type Ba8Ga16Ge30 type-I clathrate compounds prepared by the vertical bridgman method. J. Alloy. Compound. 722, 644–650 (2017).
66. A. Fonari, C. Sutton, Effective Mass Calculator, https://github.com/afonari/emc. (2012).

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Author contributions
J. Shen and Z. Fang designed the research. J. Shen, T. Xie, L. Zhang and P. Wang performed theoretical calculation, all of authors discussed the results, and J. Shen, T. Xie and Z. Fang prepared the manuscript.

Competing interests
The authors declare no competing interests.

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