High $n$-type thermoelectric power factor and efficiency in Ba$_2$BiAu

Junsoo Park, 1, 2, 3, * Yi Xia, 4, † and Vidvuds Ozoliņš 2, 3, †

1 Department of Materials Science & Engineering, UCLA, Los Angeles, CA 90095, USA
2 Department of Applied Physics, Yale University, New Haven, CT 06511, USA
3 Energy Sciences Institute, Yale University, West Haven, CT 06516, USA
4 Nanoscience and Technology Division, Argonne National Laboratory, Argonne, IL 60439, USA

(Dated: April 26, 2018)

Using first-principles density-functional theory (DFT) calculations, we predict the potential for unprecedented $zT = 5$ at 800 K in $n$-type Ba$_2$BiAu full-Heusler compound. Such a high efficiency arises from intrinsically ultralow lattice thermal conductivity coupled with very high power factor reaching 7 mW m$^{-1}$ K$^{-2}$ at 500 K. The high power factor originates from the isolated, highly dispersive conduction band with sixfold pocket multiplicity. It experiences very weak acoustic phonon scattering due to limited phase space, leading to long electron lifetime and high conductivity. The pocket multiplicity also benefits high conductivity and sustains high Seebeck coefficient. The Lorenz number at optimal doping ranges is consistently smaller than the Wiedemann-Franz value, an integral feature for $zT$ enhancement as electrons are the majority heat carriers.

PACS numbers: ******

Thermoelectric materials can be used to directly convert heat into electricity and vice versa, which has technological applications in energy harvesting and refrigeration. The indicator of thermoelectric efficiency is the dimensionless figure of merit known as $zT$. For effective commercialization of thermoelectrics, materials with $zT > 4$ are often coveted. Unfortunately, conversion efficiencies of even the best thermoelectric materials have been stagnant at $zT < 3$, only in rare cases surpassing even $zT = 2$ [1–4]. At room temperature and below, only alloys of Bi$_2$Te$_3$ have offered competitive $zT$ [5–8].

The difficulty of realizing efficient thermoelectrics can be understood from the definition $zT = \alpha^2 \sigma T / \kappa$. Here, $\sigma$ is known as the thermoelectric power factor, composed of the Seebeck coefficient ($\alpha$) and electronic conductivity ($\sigma$). The total thermal conductivity ($\kappa$) is the sum of lattice thermal conductivity ($\kappa_{\text{lat}}$) and thermal conductivity due to electrons ($\kappa_{\alpha}$). Clearly, a desirable thermoelectric material would feature high $\alpha$ and $\sigma$, while exhibiting low $\kappa$, but such a combination is inherently difficult to achieve. Researchers have discovered many methods and principles that suppress $\kappa_{\text{lat}}$ while minimally damaging the power factor [9–15]. However, achieving a simultaneously high power factor within a given material has not been as successful. The power factor itself suffers from the fact that $\sigma$ and $\alpha$ benefit from competing physical parameters. For one, high temperature often benefits $\alpha$ at relevant carrier concentrations, but at the expense of $\sigma$. Also, $\alpha$ is high at low doping levels and fades with doping, while $\sigma$ tends to monotonically increase with doping. It is then no surprise that materials with high $zT$ are very difficult to come by.

It is in this context that we present our prediction of unprecedented $zT = 5$ at 800 K in $n$-type full-Heusler Ba$_2$BiAu. This material is a member of the family of full-Heusler compounds recently discovered to be stable and to exhibit ultralow intrinsic lattice thermal conductivity arising from anharmonic rattling of heavy atoms [16]. In particular, Ba$_2$BiAu has $\kappa_{\text{lat}}$ that approaches the amorphous limit at high temperatures. Here, we predict that Ba$_2$BiAu also features high $n$-type power factor resulting in high $zT$. Via first-principles DFT calculations, we show that its lone, highly dispersive conduction band is responsible for the high power factor.

Fig. 1 is the electronic structure of Ba$_2$BiAu calculated using Quantum Espresso [17] with norm-conserving pseudopotentials and Perdew-Becke-Ernzerhof (PBE) exchange-correlation functional [18, 19]. We confirm that projector-augmented wave (PAW) [20] pseudopotentials lead to only minor changes in the band structure. Spin-orbit coupling (SOC) leads to a slight curving of the otherwise flat top-most valence band at the L-point and reduces the band gap. Most importantly it leaves the lone, highly dispersive band at the conduction band minimum (CBM) intact. This highly dispersive conduction band is a promising feature for high power factor. First, its location along the $\Gamma$-X direction gives it a sixfold pocket multiplicity. Pocket multiplicity, or band degeneracy, directly benefits $\sigma$ since carrier concentration increases for given Fermi level. Also, since the Seebeck coefficients of all pockets are weighted equally, pocket multiplicity does not harm $\alpha$ through multi-band effect [21]. Second, the band’s dispersive nature provides only a very small phase space for electron scattering by acoustic phonons. Since acoustic phonon scattering is often the most harmful process to electron transport, long electron-phonon lifetime and high mobility can be expected near the CBM.

In our calculations, we consider the two major scattering mechanisms at work in thermoelectric materials: electron-phonon scattering and ionized impurity scattering. For electron-phonon scattering, we first explicitly calculate electron-phonon interaction matrix elements over a coarse $8 \times 8 \times 8$ k-point mesh using density-
functional perturbation theory [22, 23]. We then use
maximally localized Wannier functions [24–26] for an ef-
cient interpolation of the matrix elements onto a dense
40 × 40 × 40 k-point mesh using the EPW software [27–29].
This treatment accounts for both intravalley and inter-
valley scattering. Long-ranged polar optical scattering
matrix elements are calculated separately and added to the
total matrix elements on the dense mesh [30]. With
the matrix elements, electron self-energy can be calcu-
lated, whose imaginary part is related to carrier lifetime.
For further theoretical details, refer to the supplemen-
tary materials [31]. With lifetime at hand, we employ
the Boltzmann transport equation within the relaxation
time approximation to calculate $\sigma$ and $\alpha$:

$$\sigma = \frac{1}{\Omega N_k} \sum_{\nu k} (\tau v^2)_{\nu k} \left( -\frac{\partial f}{\partial \epsilon} \right)_{\epsilon=\epsilon_{\nu k}},$$  
(1)

$$\alpha = \frac{\sigma^{-1}}{\Omega N_k} \sum_{\nu k} (\tau v^2)_{\nu k} (\epsilon_{\nu k} - \epsilon_F) \left( -\frac{\partial f}{\partial \epsilon} \right)_{\epsilon=\epsilon_{\nu k}}.$$  
(2)

Group velocity ($\nu$) and lifetime ($\tau$) depend on band $\nu$
and wavevector $k$. $\Omega$ is the primitive cell volume, $\epsilon_F$
is the Fermi level, and $f(\epsilon - \epsilon_F)$ is the Fermi-Dirac
distribution. The summations of Eqs. 1 and 2 are performed
using BoltzTraP [32] with pre-calculated electron-phonon
lifetimes.

Mobility limited by ionized impurity scattering ($\mu_{ii}$) is
estimated using the aMoBT software [33] which imple-
ments an improved form of the Brooks-Herring theory
that takes into account band non-parabolicity [34, 35].
The overall mobility ($\mu$) is obtained by combining $\mu_{ii}$
with $\mu_{eph}$ according to the Matthiesen’s rule,

$$\mu^{-1} = \mu_{eph}^{-1} + \mu_{ii}^{-1},$$  
(3)

and is used to rescale $\sigma$. We neglect SOC for the analy-
sis of scattering, since it has little effect on phonons [16]
FIG. 3. (Color online) (a) The n-type power factors and the 500 K p-type power factor versus the respective carrier concentrations. (b) The n-type power factor versus the Fermi level, where the vertical lines correspond to the intrinsic level at 300 K and the conduction band edge.

The introduction of polar optical scattering reduces what would otherwise be acoustic-phonon-limited power factor by nearly an order of magnitude. We find that ionized impurity scattering lowers the overall power factor by 25% at 300 K and by about 15% at 500 K and 800 K. Ultimately, high $zT$ requires high power factor coupled with low thermal conductivity. Ba$_2$BiAu has already been predicted to possess ultralow lattice thermal conductivity [16]: $\kappa_{\text{lat}}$ is 0.55 W m$^{-1}$ K$^{-1}$ at 300 K and 0.2 W m$^{-1}$ K$^{-1}$ at 800 K, closing on the amorphous lower limit. Because of such low $\kappa_{\text{lat}}$, heat is mainly carried by electrons ($\kappa_e \geq 1$ W m$^{-1}$ K$^{-1}$). Since $\kappa_e > \kappa_{\text{lat}}$, small Lorenz number ($L$) is indispensable for the enhancement of $zT$. This statement can be generalized beyond Ba$_2$BiAu to any wishful high $zT$ material since it must have low $\kappa_{\text{lat}}$ and high power factor. As Fig. 4 shows, our calculation indicates that throughout non-degenerate doping ranges, $L < L_{\text{WF}}$ in the favor of $zT$, where $L_{\text{WF}} = \frac{k_B^2}{e^2} \left( \frac{5}{2} + r \right)$ is the Wiedemann-Franz Lorenz number. Such a negative deviation from Wiedemann-Franz law is attributed to energy-dependent electron lifetime due to electron-phonon scattering. A simple illustration is provided by the non-degenerate approximation to the single parabolic band model, according to which [38]

$$L = \frac{k_B^2}{e^2} \left( \frac{5}{2} + r \right)$$

(4)

where the energy-dependence of scattering controls the constant $r$. For polar optical scattering, $r = \frac{2}{5}$, which leads to $L = \frac{3k_B^2}{5e^2}$, which is smaller than $L_{\text{WF}}$. If acoustic phonon scattering were to dominate, $r = -\frac{1}{2}$ and $L$ would be even lower at $\frac{2k_B^2}{e^2}$. As the Fermi level moves towards the center of the gap, $L$ increases above $L_{\text{WF}}$ as each electron carries more energy.

The combination of high power factor and low thermal conductivity in Ba$_2$BiAu leads to unprecedentedly high $n$-type $zT = 5$ at 800 K. This value is higher by far than any other 3D bulk thermoelectric to date. At 300 K, we predict $zT = 1.4$, which would also be the highest for an $n$-type material at room temperature. Fig. 5(a) shows that the peaks of $zT$ form at noticeably lower doping concentrations compared to those of the power factor. Optimal $n_e$ for $zT$ in fact corresponds to non-degenerate doping regime, as shown by Fig. 5(b). The large difference between the the optimal $n_e$ for the power factor and $zT$ is reflective of the fact that $\kappa_e$ contributes heavily to the total thermal conductivity. If $\kappa_e > \kappa_{\text{lat}}$ and $L$ is relatively constant with $n_e$, $zT$ favors lower $n_e$ where the Seebeck coefficient is high. Plus, we note that our calculations result in $zT = 0.8$ at 200 K and $zT = 0.2$ at 100 K. Though not as remarkably high as the values we highlight, they are still respectable considering the very low temperatures.

Ba$_2$BiAu has been projected to have higher $p$-type power factor than $n$-type power factor due to its flat-and-dispersive valence band [16]. Flat-and-dispersive bands in general have been associated with the insight drawn from electronic structures of low-dimensional systems [39, 40]. In superlattices, bands are dispersive in-plane, resulting in high mobility, and flat out-of-plane, resulting in step functions as density of states to the benefit of the Seebeck coefficient. Some bulk 3D compounds have been discovered to exhibit similar electronic structures where a flat band inducing high $\alpha$ and a light band inducing high $\sigma$ coexist [41].

However, according to our calculations, the highest $p$-type power factor for Ba$_2$BiAu is merely 2.5 mW m$^{-1}$ K$^{-2}$ at 500 K and the highest $p$-type $zT$ is at best 2 at 800 K. We find that the flat portion of the band offers plethora of acoustic phonon scattering space. In

FIG. 5. (Color online) (a) The $n$-type $zT$ versus electron concentration and the $p$-type $zT$ at 800 K versus hole concentration. (b) The $n$-type $zT$ versus the Fermi level.
In summary, we predict that Ba$_2$BiAu has the potential to achieve $zT = 5$ at 800 K and $zT = 1.4$ at 300 K, as per rare complementation of very high power factor, ultralow lattice thermal conductivity and small Lorenz number. We trace the origin of high power factor of Ba$_2$BiAu to the lone, highly dispersive conduction band. Due to the small phase space, electrons there experience very weak acoustic phonon scattering. Even with polar optical scattering included, the electrons in the conduction band have longer lifetimes than the holes in the valence band by factors of many. Long lifetimes and six-fold pocket multiplicity lead to high conductivity, while acoustic phonon scattering alone reduces hole lifetime at the VBM below the overall electron lifetime in CBM. Also, we find that $n$-type $\alpha$ at the optimal hole doping level is in fact lower than $p$-type $\alpha$. This shows that highly dispersive bands that minimize the acoustic phonon scattering channel can outperform flat-and-dispersive bands. On another note, the maximum $n$-type power factor and $zT$ require an order of magnitude less doping than the $p$-type counterparts. It results from the fact that the more dispersive band has higher mobility and therefore requires less carrier concentration to activate the optimal power factor and $zT$. This highlights yet another advantage of a dispersive band since the need to dope less may facilitate synthesis.

The authors acknowledge financial support from the National Science Foundation Grant DMR-1611507. This research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

---

* jsayony37@ucla.edu
† yimaverickxia@gmail.com
‡ vidvuds.ozoli@gmail.com

[1] L. Zhao, S. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid, and M. G. Kanatzidis, Nature 508, 373 (2014).

[2] K. F. Hsu, S. Loo, F. Guo, W. Chen, J. S. Dyck, C. Uher, T. Hogan, E. K. Polychroniadis, and M. G. Kanatzidis, Science 303, 818 (2004).

[3] H. Wu, L.-D. Zhao, F. Zheng, D. Wu, Y. Pei, X. Tong, M. Kanatzidis, and J. He, Nat. Comm. 5, 1 (2014).

[4] X. Shi, J. Yang, J. R. Salvador, M. Chi, J. Y. Cho, H. Wang, S. Bai, J. Yang, W. Zhang, and L. Chen, J. Amer. Chem. Soc. 133, 7837 (2011).

[5] R. Venkataramanan, E. Siivola, T. Colpitts, and B. O’Quinn, Nature 413, 597 (2001).

[6] B. Poudel, Q. Hao, Y. Ma, Y. Lan, A. Minnich, B. Yu, X. Yang, D. Wang, A. Muto, D. Vashaae, X. Chen, J. Liu, M. Dresselhaus, G. Chen, and Z. Ren, Science 320, 634 (2008).

[7] S. I. Kim, K. H. Lee, H. A. Mun, H. S. Kim, S. W. Hwang, J. W. Roh, D. J. Yang, W. H. Shin, X. S. Li, Y. H. Lee, G. J. Snyder, and S. W. Kim, Science 348, 109 (2015).

[8] L. Hu, H. Wu, T. Zhu, C. Fu, J. He, P. Ying, X. Zhao, Adv. Energy Mater. 5, 1500411 (2015).

[9] C. Vineis, A. Shakouri, A. Majumdar, and M. Kanatzidis, Adv. Mat. 22, 397039800 (2010).

[10] A. Minnich, M. S. Dresselhaus, Z. F. Ren, and G. Chen, Energy Env. Sci. 2, 466 (2009).

[11] M. Nielsen, V. Ozoliņš, and J. Heremans, Energy Env. Sci. 6, 570 (2013).

[12] D. Morelli, V. Jovovic, and J. Heremans, Phys. Rev. Lett. 101, 035901 (2008).

[13] S. Lee, K. Esfarjani, T. Luo, J. Zhou, Z. Tian, and G. Chen, Nature Comm. 5, 3525 (2014).

[14] G. P. Meisner, D. T. Morelli, S. Hu, J. Yang, and C. Uher, Phys. Rev. Lett. 80, 3551 (1998).

[15] C. W. Li, J. Hong, A. F. May, D. Bansal, S. Chi, T. Hong, G. Ehlers, and O. Delaire, Nat. Phys. 11, 1063 (2016).

[16] J. He, M. Amsler, Y. Xia, S. S. Naghavi, V. Hegde, S. Hao, S. Goedecker, V. Ozoliņš, and C. Wolverton, Phys. Rev. Lett. 117, 046602 (2016).

[17] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Scuozlo, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys. Condens. Matter 21, 395502 (19pp) (2009).

[18] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

[19] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Scuozlo, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys. Condens. Matter 21, 395502 (19pp) (2009).

[20] P. E. Blöchl, Phys. Rev. B. 50, 17953 (1994).

[21] Y. Pei, S. Xiaoya, L. Aaron, L. C. H. Wang, and G. Snyder, Nature 473, 66 (2011).

[22] S. Poncé, G. Antonius, Y. Gillet, P. Boulanger, J. L. Janssen, A. Marini, M. Côté, and X. Gonze, Phys. Rev. Lett. 90, 214304 (2014).

[23] S. Poncé, Y. Gillet, J. L. Janssen, A. Marini, M. Verstraete, and X. Gonze, J. Chem. Phys. 143, 1028137 (2015).

[24] S. Poncé, and X. Gonze, J. Chem. Phys. 12847 (1997).

[25] I. Souza, N. Marzari, and D. Vanderbilt, Phys. Rev. B. 65, 035109 (2001).

[26] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Comput. Phys. Commun. 178, 685 (2008).
[27] F. Giustino, M. L. Cohen, and S. G. Louie, Phys. Rev. B. 76, 165108 (2007).
[28] J. Noffsinger, F. Giustino, B. D. Malone, C. H. Park, S. G. Louie, and M. L. Cohen, Comput. Phys. Commun. 55, 2140 (2010).
[29] S. Ponce, E. R. Margine, C. Verdi, and F. Giustino, Comput. Phys. Commun. 55, 116 (2016).
[30] C. Verdi and F. Giustino, Phys. Rev. Lett. 115, 176401 (2015).
[31] S. materials to the main text, for figures and discussions on crystal structure, band gaps, double parabolic band model, phonons, and lattice thermal conductivity.
[32] G. K. Madsen and D. J. Singh, Comput. Phys. Commun. 175, 67 (2006).
[33] A. Faghaninia, J. W. Ager, and C. S. Lo, Phys. Rev. B. 91, 5123 (2015).
[34] D. L. Rode and S. Knight, Phys. Rev. B. 3, 2534 (1971).
[35] D. Chattopadhyay and H. J. Queisser, Rev. Mod. Phys. 53, 745 (1981).
[36] F. Tran and P. Blaha, Phys. Rev. Lett. 102, 226401 (2009).
[37] R. He, D. Kraemer, J. Mao, L. Zeng, Q. Jie, Y. Lan, C. Lie, J. Shuai, H. S. Kim, Y. Liu, D. Broido, C.-W. Chu, G. Chen, and Z. Ren, Proc. Natl. Acad. Sci. 113, 13576 (2016).
[38] G. S. Nolas, J. Sharp, and H. J. Goldsmid, Thermoelectrics (Springer, 2001).
[39] L. Hicks and M. Dresselhaus, Phys. Rev. B 47, 12727 (1993).
[40] D. Parker, X. Chen, and D. J. Singh, Phys. Rev. Lett. 119, 146691 (2013).
[41] D. I. Bilc, G. Hautier, D. Waroquiers, G.-M. Rignanese, and P. Ghosez, Phys. Rev. Lett. 114, 136601 (2015).
Supplementary Materials: High n-type thermoelectric power factor and efficiency in Ba$_2$BiAu

Junsoo Park, $^{1,2,3}$ Yi Xia, $^{4}$ and Vidvuds Ozolins$^{2,3}$

$^1$Department of Materials Science & Engineering, UCLA, Los Angeles, CA 90095, USA
$^2$Department of Applied Physics, Yale University, New Haven, CT 06511, USA
$^3$Energy Sciences Institute, Yale University, West Haven, CT 06516, USA
$^4$Nanoscience and Technology Division, Argonne National Laboratory, Argonne, IL 60439, USA

(Dated: April 26, 2018)

PACS numbers: ******

CRYSTAL & ELECTRONIC STRUCTURES

Ba$_2$BiAu is full-Heusler compound, which can be described as a rock-salt structure of Bi and Au with all eight of its diamond sublattice positions occupied by Ba. Its primitive cell is that of face-centered cubic with additional atoms in the interior. Relaxation of crystal structure and self-consistent calculation of electronic structures of the primitive cell are performed using two different schemes: using norm-conserving (NC) pseudopotentials on Quantum Espresso (QE), hereafter NC-QE, and using PAW pseudopotentials on Vienna Ab Initio Simulations Package (VASP) [1–4], hereafter PAW-VASP. PBE exchange-correlation functional is used for both cases. Plane-wave energy cut-off of 120 Ry and energy convergence threshold of $10^{-8}$ Ry are used for all NC-QE calculations. Plane-wave energy cut-off of 600 eV and energy convergence threshold of $10^{-7}$ eV are used for all PAW-VASP calculations.

The ground-state lattice parameter of Ba$_2$BiAu as calculated by NC-QE is 8.30 Å, and that by PAW-VASP is 8.42 Å. Ba$_2$BiAu has not been synthesized at all to date, so experimental data are unavailable for comparison. NC-QE and PAW-VASP yield more or less the same band structures for both compounds near their energy gaps. The 0 K band gap of Ba$_2$BaAu is 0.44 eV when calculated with plain NC-QE and 0.45 eV when calculated with PAW-VASP. With Heyd-Scuza-Ernzerhof (HSE) correction [5, 6], the gap increases to 0.74 eV. With spin-orbital coupling but without HSE06, $\Delta E_g$ is 0.25 eV. The most accurate value is likely predicted by the mBJ functional with SOC, which yields $\Delta E_g$ of 0.56 eV. It is this value we use for transport calculations.

Ba$_2$BiAu features pipe-like isoenergy surface at the valence band maximum, reflective of its flat-and-dispersive nature. Effective mass ($m$) is large along the pipes, corresponding to the flat direction, and small around the pipes. On the other hand, the isoenergy surface at the CBM is a set of oblates poised in the middle of the six $\Gamma$-X directions. These oblates reflect that $m$ is very small along most of the directions, characteristic of the dispersive conduction band.

ELECTRON-PHONON SCATTERING

Since an accurate description of electron-phonon scattering is critical for thermoelectric performance, we perform rigorous matrix element calculations. Electron-phonon interaction matrix elements and corresponding electron self-energies are treated within the framework of harmonic phonon perturbation to electronic states. Electron-phonon scattering rate (inverse lifetime) dependent on band $\nu$ and phonon mode $\lambda$ is calculated as

$$\tau^{-1}_{\text{eph},\nu\lambda k} = \frac{2}{R} \Sigma_{\text{Im},\nu\lambda k}$$  

Here, $\Sigma_{\text{Im}}$ is the imaginary part of electron self-energy, a.k.a., electron linewidth, defined as

FIG. S1. (Color online) a) The unit cell. b) The primitive cell. Ba is green, Bi is purple, and Au is gold.

FIG. S2. (Color online) Isoenergy surfaces of the topmost valence band (left) and lowermost conduction bands (right) of Ba$_2$BiAu near their extrema.
\[ \Sigma_{\text{im}, \nu'\lambda k} = \frac{\pi}{N_q} \sum_{\nu'q} |g_{\nu'\nu\lambda}(k, q)|^2 \times \left[ (b(\omega_{\lambda q}, T) + f(\epsilon_{\nu'k+q}, \epsilon_F, T)) \delta(\epsilon_{\nu k} + \omega_{\lambda q} - \epsilon_{\nu'k+q})d\epsilon \right. \\
+ \left. (b(\omega_{\lambda q}, T) + 1 - f(\epsilon_{\nu'k+q}, \epsilon_F, T)) \delta(\epsilon_{\nu k} - \omega_{\lambda q} - \epsilon_{\nu'k+q})d\epsilon \right] \]  
\tag{S2} 

where \( \omega \) is phonon frequency, \( N_q \) is the number of \( q \)-points, \( \delta \) are energy-conserving delta functions, \( b \) is phonon population given by the Bose-Einstein distribution, and \( f \) is electron population given by the Fermi-Dirac distribution. The most important ingredient in the evaluation of \( \Sigma_{\text{im}} \) is mode-and-band-resolved electron-phonon interaction matrix elements:

\[ g_{\nu'\nu\lambda}(k, q) = \sqrt{\frac{1}{2m_0w_{\lambda q}}} \left\langle \psi^{(0)}_{\lambda k+q} \left| \partial V_{\lambda q} \right| \psi^{(0)}_{\nu k} \right\rangle. \]  
\tag{S3} 

In the above expression, \( \psi^{(0)} \) is the ground-state wavefunction and \( \partial V \) is the perturbation due to atomic displacement by harmonic phonons. Since explicit calculation of a matrix element of the form of Eq. S3 is computationally expensive, a reasonable approach is to compute it on a coarse mesh and then to interpolate it onto a much denser mesh throughout the Brillouin zone. To accomplish this, we use the EPW software, which performs the interpolation via maximally localized Wannier functions (MLWF). Polar optical scattering cannot be treated with Wannier interpolation due to the long-ranged nature of the interaction and the localized nature of MLWF. Therefore, they are calculated separately and then added to the total matrix elements on the dense mesh. The long-ranged polar optical scattering matrix elements are given by

\[ g_{\nu'\nu\lambda}^L(k, q) = i \sum_a \sqrt{\frac{1}{2M_0w_{\lambda q}}} \sum_{\mathbf{G} \neq -q} \frac{(q + \mathbf{G}) \cdot Z^* \cdot e_{\alpha\lambda q}}{(q + \mathbf{G}) \cdot \epsilon^\infty \cdot (q + \mathbf{G})} \left\langle \psi_{\nu'k+q}^{(0)} \left| e^{i(q+\mathbf{G})\cdot \mathbf{r}} \right| \psi_{\nu k}^{(0)} \right\rangle, \]  
\tag{S4} 

where \( Z^* \) is the Born effective charge tensor, \( \epsilon^\infty \) is the high-frequency dielectric permittivity tensor, \( M_0 \) is the mass of atom \( a \), \( \mathbf{e} \) is phonon eigenvector, \( \mathbf{G} \) is the reciprocal lattice vector, and \( \mathbf{r} \) is atomic position vector.

Since EPW runs in conjunction with QE and is compatible only with NC pseudopotentials, NC-QE rather than VASP is our DFT tool of choice for all calculations involved in electron-phonon scattering. In preparation for electron-phonon calculations, we first perform structural relaxation and self-consistent energy minimization. Convergence is safely achieved with a 40 \( \times \) 40 \( \times \) 40 \( k \)-point mesh. We then compute harmonic phonons and their interaction matrices with electrons using a 8 \( \times \) 8 \( \times \) 8 \( k \)-point mesh for electrons and a 4 \( \times \) 4 \( \times \) 4 \( q \)-point mesh for phonons by density functional perturbation theory. Finally, we interpolate the matrix elements onto 40 \( \times \) 40 \( \times \) 40 \( k \)-point mesh and \( q \)-point mesh. We confirm the localization of the Wannier Hamiltonian, the real-space dynamical matrix and electron-phonon interaction matrix elements from their decay over short ranges, as shown in Fig. S3. We also confirm the quality of Wannier interpolation by reconstructing the band structure from interpolation and matching it with the self-consistently calculated band structure.

Carrier conductivity and the Seebeck coefficients are provided in Fig. S4.

**FIG. S3.** (Color online) **a** Localization of Wannier Hamiltonian and dynamical matrix elements, normalized to 1, of Ba\(_2\)Bi\(_2\)Te\(_3\). **b** Log-scale decay of electron-phonon interaction matrix elements.

**FIG. S4.** (Color online) **a** The absolute \( n \)-type Seebeck coefficients and 500 K \( p \)-type Seebeck coefficient versus the respective carrier concentrations. **b** The \( n \)-type conductivity.
He *et al* [7] have investigated phonons and intrinsically ultralow lattice thermal conductivity of Ba$_2$BiAu using state-of-the-art computational methods. We follow the same steps and arrive at identical results. For convenience, we provide our reproduction of the $\kappa_{\text{lat}}$ prediction in Fig. S5.

![Graph showing lattice thermal conductivity of Ba$_2$BiAu.](image)

**FIG. S5.** Lattice thermal conductivity of Ba$_2$BiAu.

[1] G. Kresse and J. Hafner, Phys. Rev. B. **47**, 558 (1993).
[2] G. Kresse and J. Hafner, Phys. Rev. B. **49**, 14251 (1994).
[3] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[4] G. Kresse and J. Furthmüller, Phys. Rev. B. **54**, 11169 (1996).
[5] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
[6] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **121**, 1187 (2004).
[7] J. He, M. Amsler, Y. Xia, S. S. Naghavi, V. Hegde, S. Hao, S. Goedecker, V. Ozoliņš, and C. Wolverton, Phys. Rev. Lett. **117**, 046602 (2016).