Remarkable thermoelectric performance in BaPdS$_2$ via pudding-mold band structure and ultralow lattice thermal conductivity

Eric B. Isaacs and Chris Wolverton

Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, USA

(Dated: October 23, 2018)

Efficient thermoelectric materials require a rare and contraindicated combination of materials properties: large electrical conductivity, large Seebeck coefficient, and low thermal conductivity. One strategy to achieve the first two properties is via low-energy electronic bands containing both flat and dispersive parts in different regions of crystal momentum space, known as a pudding-mold band structure. Here, we illustrate that BaPdS$_2$ successfully achieves the pudding-mold band structure, contributing to a large thermoelectric power factor, due to its anisotropic crystal structure containing zig-zag chains of edge-sharing square planar PdS$_4$ units. In addition, BaPdS$_2$ exhibits ultralow lattice thermal conductivity, and thus also achieves the third property, due to extremely soft and anharmonic interactions in its transverse acoustic phonon branch. We predict a remarkably large thermoelectric figure of merit, with peak values between 2 and 3 for two of the three crystallographic directions, suggesting BaPdS$_2$ warrants experimental investigation.

I. INTRODUCTION

The figure of merit for a thermoelectric material, which can convert a temperature gradient into electrical current, is

$$ZT = \frac{S^2 \sigma}{\kappa_{el} + \kappa_L} T,$$

where $S$, $\sigma$, $T$, $\kappa_{el}$, and $\kappa_L$ are the Seebeck coefficient, electrical conductivity, temperature, electrical contribution to thermal conductivity, and lattice contribution to thermal conductivity, respectively. One strategy to achieve a large $ZT$ is via engineering the electronic band structure, i.e., the electron energy $\epsilon$ as a function of crystal momentum $\mathbf{k}$. In particular, a band with both flat (small $\nabla_k \epsilon$) and dispersive (large $\nabla_k \epsilon$) parts along a direction in $\mathbf{k}$-space has been shown to enhance $\sigma S^2$ if the electron chemical potential $\mu$ lies at an energy separating the two regions. In such a “pudding-mold” band structure, the band velocity difference leads to large $S$, and large $\sigma$ is achieved due to the dispersive part of the band and a large Fermi surface. More generally, one can consider a broader definition of a pudding-mold band structure in which the flat and dispersive regions can along different directions in $\mathbf{k}$-space, which naturally occurs for low-dimensional bulk and nanostructured crystals. The pudding-mold band structure has been used to explain the promising thermoelectric performance of Na$_x$CoO$_2$ and recently-proposed Fe-based Heusler compounds among others.

Recently, the promising thermoelectric performance of several Pd oxide compounds has been attributed in part to the pudding-mold band structure. The layered compound PbPdO$_2$, for example, exhibits a large Seebeck coefficient of 175 $\mu$V/K at 600 K when hole doped. Based on first-principles calculations, hole-doped Bi$_2$PdO$_4$ was predicted to exhibit high power factor ($\sigma S^2$) in addition to low $\kappa_L$. In both of these compounds, achieving the pudding-mold band structure appears to be connected to the presence of square planar Pd$^{2+}$. Based on this observation, we previously developed an inverse band structure design approach based on a materials database screening to search for other square planar compounds achieving the pudding-mold band structure. Although several chemistries were considered, we focused on oxide materials such as Ba$_2$PdO$_3$ and La$_4$PdO$_7$ in order to validate the approach.

The thermoelectric efficiency of oxides is often limited by (1) large $\kappa_L$, stemming from the low atomic mass of oxygen and rigid chemical bonding, and (2) low carrier mobility. Therefore, in this work, we turn our attention to chalcogenide materials. Chalcogenides comprise many of the most-investigated and highest-performance thermoelectrics, such as PbTe, Bi$_2$Te$_3$, SnSe, Cu$_2$(S/Se)$_3$, and La$_3$-Te$_4$. We investigate a chalcogenide material based on square planar Pd, namely BaPdS$_2$, with the aim of achieving low $\kappa_L$ in addition to pudding-mold band structure. BaPdS$_2$ is the only such square planar chalcogenide identified by our previous inverse band structure design approach other than metallic EuPd$_3$S$_2$ and the binaries PdS$_2$ and PdSe$_2$. Although BaPdS$_2$ was first synthesized in 1986, it has not been explored as a thermoelectric material to the best of our knowledge. The presence of heavy Ba, in addition to the lack of oxygen, leads to the potential for low $\kappa_L$. Using electronic structure and transport calculations based on the density functional theory, we find that BaPdS$_2$ exhibits (1) a pudding-mold band structure for $p$-type doping, (2) large power factor for both $n$- and $p$-type doping, (3) ultraslow $\kappa_L$ due to extremely soft and anharmonic bonding, and (4) highly-anisotropic electronic and thermal transport behavior. We find remarkable predicted thermoelectric performance, with $ZT$ larger than 2 in certain crystallographic directions at high temperature, assuming optimal doping and using a reasonable value of electronic relaxation time $\tau$ (5 fs). Based on these results, we suggest BaPdS$_2$ warrants experimental investigation.
II. COMPUTATIONAL DETAILS

We perform density functional theory calculations using the generalized gradient approximation and the projector augmented wave method (Ba, Pd, and S potentials) in the Vienna ab initio simulation package (VASP). A plane wave basis with 500 eV kinetic energy cutoff and uniform k-meshes with \( \geq 700 \) k-points per \( \text{Å}^{-3} \) are employed. The ionic forces and total energy are converged to \( 10^{-3} \text{ eV}/\text{Å} \) and \( 10^{-6} \text{ eV} \), respectively. High-symmetry k- and q-point paths are based on the conventions of Setyawan et al.

Semiclassical electronic transport calculations within the constant relaxation time approximation are performed using BOLTZTRAP with k-point density of 3,500/Å\(^3\). Phonon calculations are performed using the direct approach in PHONOPY with a 192-atom supercell chosen to be approximately cubic based on the algorithm of Erhart et al. as implemented in ASE. The mode Grüneisen parameter is computed using a ±0.3% volume difference. \( \kappa_L \) is computed via the Debye-Callaway model and compared to that of the minimum thermal conductivity model of Cahill et al. \( \kappa_d \) is computed via the Wiedemann-Franz law. Additional details on the electronic and thermal transport calculations are included in the Supplemental Material.

III. RESULTS AND DISCUSSION

BaPdS\(_2\), shown in Fig. 1(a) and Fig. 1(b), has a C-centered orthorhombic unit cell with space group Cmcm. Isostructural to BaNiO\(_2\), it consists of 1D chains of edge-sharing PdS\(_4\) square planar units (corresponding to a PdS\(_2\) composition) connected in a zig-zag pattern. The computed lattice parameters, atomic positions, and formation energy are in good agreement with experimental values, as discussed in the Supplemental Material. The electronic band structure of BaPdS\(_2\) is shown in Fig. 1(c). The valence band, which consists primarily of Pd d states, exhibits a pudding-mold band structure. It is dispersive in the direction along the 1D chains (e.g., \( \Gamma-Z \)) and flat along other directions (e.g., \( \Gamma-X \) and \( \Gamma-Y \)). In order words, the pudding-mold band structure is closely related to the highly-anisotropic crystal structure of BaPdS\(_2\). We do not find a pudding-mold band structure for the conduction band, which consists of a hybridization of Pd d and S p orbitals. We note that an additional conduction band minimum between S and R is close in energy (\( \sim 130 \text{ meV} \)) to the band edge at \( \Gamma \).

The band structure of BaPdS\(_2\) leads to notable electronic transport properties. Figure 2(a) illustrates the behavior of the average (over Cartesian directions) of \( \sigma S^2/\tau \) as a function of carrier concentration for several temperatures. Results for BaPdS\(_2\) are shown in comparison to those of SnSe, a high-performing thermoelectric material. BaPdS\(_2\) achieves comparable p-type power factor behavior to SnSe, albeit at larger (though still reasonable) doping values. For example, at 700 K, the maximum predicted p-type \( \sigma S^2/\tau \) is \( \sim 3 \times 10^{11} \text{ W/(m-K}^2\text{-s)} \) for both BaPdS\(_2\) (for \( 7 \times 10^{20} \) holes/cm\(^3\)) and SnSe (for \( 3 \times 10^{20} \) holes/cm\(^3\)). We also note that the p-type power factor behavior exhibits significantly less temperature dependence for BaPdS\(_2\) than for SnSe. Although the conduction band does not exhibit pudding-mold qualities, we find even larger \( \sigma S^2/\tau \) for n-type doping, though smaller than the corresponding SnSe behavior. For example, the peak n-type \( \sigma S^2/\tau \) for BaPdS\(_2\) at 700 K is \( 5.3 \times 10^{11} \text{ W/(m-K}^2\text{-s)} \), occurring at a doping value of \( \sim 5.5 \times 10^{20} \) electrons/cm\(^3\); SnSe exhibits a significantly larger peak n-type \( \sigma S^2/\tau \) of \( 8.4 \times 10^{11} \text{ W/(m-K}^2\text{-s)} \) at around the same doping magnitude. The appreciable n-type power factor behavior for BaPdS\(_2\) likely stems from the band convergence, i.e., the small energy separation between the conduction band minima (1) at \( \Gamma \) and (2) between S and R.

FIG. 1. Orthographic projection of the crystal structure of BaPdS\(_2\) along the (a) c and (b) a axes of the conventional unit cell (red dashed lines). The green, gray, and yellow circles represent Ba, Pd, and S atoms, respectively. Black lines indicate the Pd–S bonds of the square planar units. (c) The electronic bands of BaPdS\(_2\) colored by the Pd d character of the electronic states. The black dashed line corresponds to the valence band minimum, and the gray horizontal dotted lines indicate the \( \pm 10^{20} \) cm\(^{-3}\) doping levels.
Due to the structural anisotropy, the power factor behavior for BaPdS$_2$ is highly anisotropic. We illustrate the power factor behavior at 700 K, for example, in Fig. 2(b) for each direction. For hole doping, $\sigma S^2/\tau$ is only appreciable along the $z$ direction (i.e., along the 1D chains), which is consistent with the pudding-mold band structure. In contrast, for electron doping, large $\sigma S^2/\tau$ is observed in both the $z$ and $x$ directions. A rationalization for the lower $n$-type power factor behavior in the $y$ direction is discussed in the Supporting Information.

![FIG. 2. (a) Power factor divided by electronic relaxation time as a function of carrier concentration for BaPdS$_2$ (lines) and SnSe (circles), averaged over the $x$, $y$, and $z$ directions, for several values of $T$. (b) $T = 700$ K power factor divided by electronic relaxation time versus carrier concentration in each direction, in addition to the average, for BaPdS$_2$.](image)

Having established the promising predicted electronic transport properties of BaPdS$_2$, we now turn our attention to thermal transport. The phonon dispersion of BaPdS$_2$ is shown in Fig. 3(a). Low-frequency optical modes, primarily involving vibration of the heavy Ba atoms, are observed in the $\sim 30$–110 cm$^{-1}$ frequency range. For each acoustic branch, we compute the group velocity in the long-wavelength limit ($v_x$, $v_y$, and $v_z$) and Debye temperature ($\Theta_{\Gamma X}$, $\Theta_{\Gamma Y}$, and $\Theta_{\Gamma Z}$) for each direction, as shown in Table I. Here, we define $\Theta$ as the acoustic phonon frequency at the zone boundary, and the acoustic branch definitions are given in the Supplemental Material. BaPdS$_2$ is a very soft material, exhibiting low group velocities (0.5–4.1 km/s) and Debye tempera-

![FIG. 3. (a) BaPdS$_2$ phonon bands colored by Ba contribution to the phonon eigenvector. (b) The low-frequency portion of the phonon dispersion with bands colored by the magnitude of the mode Gr"uneisen parameter. (c) Dispersion of the mode Gr"uneisen parameter $\gamma_{q\nu}$ for the acoustic branches. Due to the large $\gamma_{q\nu}$ values for the TA branch along $\Gamma$–X, we use a broken $\gamma_{q\nu}$ axis for clarity.](image)
For comparison, $v$ of 1.0–2.9 and $\Theta$ of 19–72 are found in SnSe. The transverse acoustic (TA) branch of BaPdS$_2$ is particular soft, with $v = 0.5$ km/s (0.8 km/s) and $\Theta = 43$ K (42 K) along the $x$ ($z$) direction. Animations of the TA phonons along $X$ (featuring rigid PdS$_2$ chains sliding in the $z$ direction with respect to the others) and along $Z$ (featuring oscillations of the individual PdS$_2$ chains in the $x$ direction) are included in the Supplemental Material. We note that the behavior of the TA branch is significantly harder along the $y$ direction in terms of the group velocity (1.9 km/s), though not the Debye temperature (49 K). Corresponding to PdS$_2$ chains sliding in the $z$ direction, the TA branch along $Y$ corresponds to a similar atomic motion to that along $X$; the significantly larger inter-chain distance in the $y$ direction (10.8 Å) compared to that in $x$ direction (6.9 Å) may be responsible for the very different phonon properties.

| Branch | $\gamma_{\text{all}}$ | $\gamma_{\text{X}}$ | $\gamma_{\text{Y}}$ | $\gamma_{\text{Z}}$ | $\gamma_{\text{X}}$ | $\gamma_{\text{Y}}$ | $\gamma_{\text{Z}}$ |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| TA     | 25.5            | 80.3            | 0.3             | 22.8            | 5.1             | 2.7             | 1.0             |
| TA'    | 2.8             | 2.6             | 3.1             | 1.0             | 1.1             | 2.4             | 2.7             |
| LA     | 2.3             | 2.1             | 1.2             | 4.0             | 5.9             | 1.3             | 3.3             |
| Avg.   | 10.2            | 28.3            | 1.5             | 9.3             | 4.1             | 2.1             | 2.3             |

TABLE II. Averages (computed as $\sqrt{\langle \gamma^2 \rangle}$) of mode Grüneisen parameter $\gamma_{\text{q}}$ for BaPdS$_2$ and SnSe for different acoustic branches and directions. For BaPdS$_2$, the average over the entire high-symmetry path in the Brillouin zone is also given as $\gamma_{\text{all}}$.

To acquire a baseline assessment for the overall magnitude of the anharmonicity, i.e., the phonon-phonon scattering strength, we compute the mode Grüneisen parameter

$$\gamma_{\text{q}} = -\frac{\partial \omega_{\text{q}}/\omega_{\text{q}}}{\partial V/V},$$

where $V$ is the volume and $\omega_{\text{q}}$ is the phonon frequency for crystal momentum $\mathbf{q}$ and branch $\nu$. The low-frequency phonons of BaPdS$_2$, colored by $|\gamma|$, are shown in Fig. 3(b), whereas the full dispersion of $\gamma_{\text{q}}$ for the acoustic branches is included in Fig. 3(c). The most prominent feature is that BaPdS$_2$ has gigantic $\gamma_{\text{q}}$ for the TA branch along $\Gamma$–$X$ (values up to $\sim 125$) and $\Gamma$–$Z$ (values up to $\sim 35$), which indicates extremely anharmonic interactions for this acoustic branch in BaPdS$_2$. We perform tests to confirm the large computed $\gamma_{\text{q}}$ are not a numerical artifact, as discussed in the Supplemental Material. Averages of the mode Grüneisen parameter for each acoustic branch of BaPdS$_2$, averaged over $\Gamma$–$X$, $\Gamma$–$Y$, $\Gamma$–$Z$, and the full high-symmetry path in the Brillouin zone, are shown in Table II, in which we also compare to literature results for SnSe. The average $\gamma_{\text{q}}$ for the TA branch of BaPdS$_2$ is 80.3 in the $x$ direction and 22.8 in the $z$ direction, compared to much smaller (less anharmonic) values of 5.1 and 1.0 for SnSe in the corresponding directions. We note that a key exception to the large anharmonicity of the TA branch of BaPdS$_2$ is along the $y$ direction, for which the average $\gamma_{\text{q}}$ is only 0.3, as compared to 2.7 for SnSe. In other words, the TA branch of BaPdS$_2$ is not only harder in the $y$ direction than the other directions, but also much less anharmonic. Although the most remarkable finding is the extremely large $\gamma_{\text{q}}$ for the TA branch, we also find significant anharmonicity for other phonon branches. For example, the TA′ (LA) branch exhibits appreciable $\gamma_{\text{q}}$ of 1.0–3.1 (1.2–4.0), as compared to 1.1–2.7 (1.3–5.9) for SnSe. Large anharmonicity is also found in the lowest-frequency optical branch, with mode Grüneisen parameter values as large as $\sim 12$, as shown in Fig. 3(b). This branch corresponds to oscillation of the Ba sublattice with respect to the PdS$_2$ chains in the $z$ direction.

We employ the Debye-Callaway model, an approximate model taking into account normal and Umklapp acoustic phonon-phonon scattering via the mode Grüneisen parameter, as a means to estimate the lattice thermal conductivity of BaPdS$_2$. We note that the low-frequency optical phonons with large $\gamma_{\text{q}}$, not taken into account in the Debye-Callaway model, may further lower $\kappa_L$ compared to the values reported here. The contributions of each acoustic phonon branch to $\kappa_L$ as a function of $T$ in the $x$, $y$, and $z$ directions are shown in Fig. 4(d)–4(f), the combination of which is the least anharmonic. Like the power factor, the thermal transport is highly anisotropic: in the $x$ direction, $\kappa_L$ is much larger (values of 4–8 W/m·K) than in the other directions, stemming primarily from the small $\gamma_{y}$ of 0.3 for the TA branch, as discussed above. In the $x$ and $z$ (but not $y$) directions, BaPdS$_2$ achieves minimum possible $\kappa_L$, shown as red lines in Fig. 4(a)–4(c), estimated from the model of Cahill et al. Overall, BaPdS$_2$ is predicted to exhibit remarkably poor thermal transport in directions other than $y$.

As illustrated in Fig. 4(d)–4(f), the combination of large power factor and low $\kappa_L$ leads to impressive figure of merit for BaPdS$_2$, particularly in the $x$ direction for electron doping and in the $z$ direction for both electron and hole doping. At high temperature, we find peak $ZT$ values of nearly 3 in the $x$ direction (for $6.0 \times 10^{19}$ electrons/cm$^3$) and values of nearly 2.3 in the $z$ direction (for $1.1 \times 10^{20}$ electrons/cm$^3$ or $1.6 \times 10^{20}$ holes/cm$^3$). In contrast, much smaller peak $ZT$ (< 1) is observed for BaPdS$_2$ in the $y$ direction, due to the smaller power factor and larger $\kappa_L$. In order to obtain the predicted $ZT$ values discussed above, we have chosen an electronic relaxation time ($\tau$) of 5 fs. While an ab initio estimation of $\tau$ (e.g., from electron-phonon scattering calculations)
FIG. 4. (a)–(c) Stacked plots of BaPdS$_2$ acoustic branch contributions to $\kappa_L$ versus $T$ computed via the Debye-Callaway model for the (a) $x$, (b) $y$, and (c) $z$ directions, respectively. Red lines indicate the minimum $\kappa_L$ of the Cahill model. (d)–(f) $ZT$ as a function of carrier concentration for different $T$ in the (d) $x$, (e) $y$, and (f) $z$ directions, respectively. Values are shown for $\tau = 5$ fs.

will be important future work, we note that 5 fs is reasonable in terms of the order of magnitude and can be considered a conservative estimate based on previous works.\cite{Takahashi2017, Hui2019, Yang2020} Even with a less optimistic guess for the electronic scattering time, we still find quite large values for the thermoelectric figure of merit, albeit at larger doping. For example, assuming $\tau = 1$ fs, a peak $ZT$ of 1.3 is achieved in the $x$ direction for $2.0 \times 10^{20}$ electrons/cm$^3$. Therefore, even with the uncertainty in $\tau$, our results strongly suggest BaPdS$_2$ merits experimental investigation.

IV. CONCLUSIONS

BaPdS$_2$, previously identified by our inverse band structure design approach, is a square planar sulfide material with remarkable, anisotropic thermoelectric properties. Due to a pudding-mold valence band structure and multiple conduction bands, BaPdS$_2$ exhibits impressive power factor behavior in two of the crystallographic directions. With heavy Ba atoms and extremely soft and anharmonic bonding, BaPdS$_2$ achieves ultralow lattice thermal conductivity in the $x$ and $z$ directions. We predict peak $ZT$ values of 2–3 in the $x$ direction ($n$-type) and the $z$ direction ($n$- and $p$-type) for an electronic relaxation time of 5 fs. Our results strongly suggest BaPdS$_2$ warrants experimental investigation for its remarkable electronic, thermal transport, and thermoelectric properties.

ACKNOWLEDGMENTS

We acknowledge support from the U.S. Department of Energy under Contract de-sc0014520. Computational resources were provided by the National Energy Research Scientific Computing Center (U.S. Department of Energy Contract DE-AC02-05CH11231) and the Extreme Science and Engineering Discovery Environment (National Science Foundation Contract ACI-1548562).

---

1 H. J. Goldsmid, Introduction to Thermoelectricity, Springer Series in Materials Science, Vol. 121 (Springer, Berlin, Heidelberg, 2010).

2 A. Zevakhin, D. M. Smiadak, J. L. Blackburn, A. J. Ferguson, M. L. Chabinyc, O. Delaire, J. Wang, K. Kovnir, J. Martin, L. T. Schelhas, T. D. Sparks, S. D. Kang, M. T. Dylla, G. J. Snyder, B. R. Ortiz, and E. S. Toberer, Appl. Phys. Rev. 5, 021303 (2018).

3 Y. Pei, H. Wang, and G. J. Snyder, Adv. Mater. 24, 6125 (2012).

4 K. Kuroki and R. Arita, J. Phys. Soc. Jpn. 76, 083707 (2007).

5 L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B 47, 12727 (1993).

6 L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B 47, 16631 (1993).

7 H. Usui and K. Kuroki, J. Appl. Phys. 121, 165101 (2017).

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

9 K. Kutorasinski, B. Wiendlocha, S. Kaprzyk, and J. Tobola, Phys. Rev. B 91, 205201 (2015).

10 Z. Wang, C. Fan, Z. Shen, C. Hua, Q. Hu, F. Sheng, Y. Lu, H. Fang, Z. Qiu, J. Lu, Z. Liu, W. Liu, Y. Huang, Z.-A. Xu, D. W. Shen, and Y. Zheng, Nat. Commun. 9, 47 (2018).
