BaBi$_2$O$_6$: a Promising $n$-Type Thermoelectric Oxide with the PbSb$_2$O$_6$ Crystal Structure —
Supplementary Information

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Convergence

Figure S1: The total VASP energies of BaBi$_2$O$_6$ against (a) plane-wave energy cut-off and (b) k-point grid. The value converged to 10 meV atom$^{-1}$ is highlighted in orange.

Figure S2: Convergence of the lattice thermal conductivity of BaBi$_2$O$_6$ against q-point mesh side broken down by lattice direction. Lattice thermal conductivities are converged to 0.01 W m$^{-1}$ K$^{-1}$ by the used 24 $\times$ 24 $\times$ 24 q-point mesh.
BaBi$_2$O$_6$ Brillouin Zone

Figure S3: First Brillouin zone of BaBi$_2$O$_6$ (space group P$\overline{3}$1m (162)), adapted from the Bilbao Crystallographic Server.$^1$ The Bradley–Cracknell paths$^2$ used in the electron and phonon dispersions (main text Figures 5(b) and 8(a)) are shown in orange.
Defects

Table S1: The formation energies of BaBi$_2$O$_6$ and its competing phases using HSE06

<table>
<thead>
<tr>
<th>Phase</th>
<th>$E_f$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$_2$Bi$_3$</td>
<td>-4.363</td>
</tr>
<tr>
<td>Ba$_4$Bi$_3$</td>
<td>-7.391</td>
</tr>
<tr>
<td>BaO</td>
<td>-5.069</td>
</tr>
<tr>
<td>BaO$_2$</td>
<td>-5.736</td>
</tr>
<tr>
<td>BiO$_2$</td>
<td>-2.856</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>-5.801</td>
</tr>
<tr>
<td>Bi$_4$O$_7$</td>
<td>-11.71</td>
</tr>
<tr>
<td>Ba$_2$Bi$_2$O$_5$</td>
<td>-17.26</td>
</tr>
<tr>
<td>BaBi$_2$O$_6$</td>
<td>-12.19</td>
</tr>
</tbody>
</table>

Table S2: The chemical potential limits of the stable region of BaBi$_2$O$_6$ under O-poor conditions using HSE06, also illustrated in main text Figure 9

<table>
<thead>
<tr>
<th>Competing Phases</th>
<th>$\mu_{Ba}$ (eV)</th>
<th>$\mu_{Bi}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
<td>Bi$_2$O$_3$</td>
<td>-6.335</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>Ba$_2$Bi$_2$O$_5$</td>
<td>-5.398</td>
</tr>
<tr>
<td>Ba$_2$Bi$_2$O$_5$</td>
<td>BaO$_2$</td>
<td>-5.290</td>
</tr>
<tr>
<td>BaO$_2$</td>
<td>Elements</td>
<td>-5.736</td>
</tr>
</tbody>
</table>
Figure S4: Concentrations of the different charge states for (a) La₈₀Ba₂ and (b) F₀ in BaBi₂O₆. The x-axis value shows the total dopant amount that would be needed to get the carrier concentration given by the orange line. At high carrier concentrations, these values differ because a significant number of dopant atoms form neutral defects (blue line).
Oxygen Interstitial

Figure S5: Relaxed O interstitial, which forms a peroxide-like species. Ba is green, Bi grey and O red, except for the peroxide-like defect in yellow.
**AMSET inputs**

**Table S3:** The $k$-point meshes used in the density of states (DoS), the interpolated DoS used in AMSET, density functional perturbation theory (DFPT) and optics calculations for BaBi$_2$O$_6$. The layers are in the $ab$ plane. The high-frequency dielectric constant was calculated from the optics calculation, the ionic dielectric constant, elastic constant, piezoelectric constant (of 0) and polar optical phonon frequency were calculated from DFPT. The static dielectric constant is the sum of the high-frequency and ionic dielectric constants.

<table>
<thead>
<tr>
<th>Calculation</th>
<th>DoS</th>
<th>Interpolated DoS</th>
<th>DFPT</th>
<th>Optics</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$-point mesh</td>
<td>$12 \times 12 \times 12$</td>
<td>$91 \times 91 \times 75$</td>
<td>$14 \times 14 \times 12$</td>
<td>$10 \times 10 \times 9$</td>
</tr>
</tbody>
</table>

High-frequency dielectric constant ($\epsilon_0$) =

$$
\begin{bmatrix}
6.90 & 0 & 0 \\
0 & 6.90 & 0 \\
0 & 0 & 6.25
\end{bmatrix}
$$

Static dielectric constant ($\epsilon_0$) =

$$
\begin{bmatrix}
17.26 & 0 & 0 \\
0 & 17.18 & 0 \\
0 & 0 & 9.79
\end{bmatrix}
$$

Elastic constant (GPa) =

$$
\begin{bmatrix}
173 & 11 & 82 & 0 & 0 & 79 \\
11 & 174 & 82 & 0 & 0 & -79 \\
82 & 82 & 80 & 0 & 0 & 0 \\
0 & 0 & 0 & 82 & -79 & 0 \\
0 & 0 & 0 & -79 & 180 & 0 \\
79 & -79 & 0 & 0 & 0 & 108
\end{bmatrix}
$$

Polar optical phonon frequency (THz) = 8.70
Mobility

**Figure S6:** Electron mobility in the in-plane direction against temperature at various doping concentrations.
References
