Vacancy-ordered Double Perovskites $A_2BX_6$ ($A = \text{Cs, Pt, Pd, Te, Sn, X = I}$): An Emerging Class of Thermoelectric Materials

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Abstract

Vacancy-ordered double perovskites ($A_2BX_6$), being one of the environmentally friendly and stable alternatives to lead halide perovskites, have garnered considerable research attention in the scientific community. However, their thermal transport has not been explored much despite their potential applications. Here, we explore $A_2BX_6$ ($A = \text{Cs, Pd, Te, Sn}, X = \text{I}$) as potential thermoelectric materials using state-of-the-art first-principles methodologies, viz., density functional theory (DFT) combined with many-body perturbation theory ($G_0W_0$) and spin-orbit coupling (SOC). The phonon dispersion plots and Poisson’s and Pugh’s ratios show the dynamical and mechanical stability of this class of perovskites. The absence of polyhedral connectivity in vacancy-ordered perovskites gives rise to additional degrees of freedom leading to lattice anharmonicity. The presence of anharmonic lattice dynamics leads to strong electron-phonon coupling, which is well captured by Fröhlich mesoscopic model to investigate the interaction of longitudinal optical phonon modes with the carriers that strongly influence the carrier mobility. The lattice anharmonicity is further studied using $ab\ initio$ molecular dynamics simulations and electron localization function. The maximum anharmonicity is observed in $\text{Cs}_2\text{PtI}_6$, followed by $\text{Cs}_2\text{PdI}_6$, $\text{Cs}_2\text{TeI}_6$ and $\text{Cs}_2\text{SnI}_6$. Also, the computed average thermoelectric figure of merit ($zT$) for $\text{Cs}_2\text{PtI}_6$, $\text{Cs}_2\text{PdI}_6$, $\text{Cs}_2\text{TeI}_6$ and $\text{Cs}_2\text{SnI}_6$ are 0.88, 0.85, 0.95 and 0.78, respectively, which reveals their promising renewable energy applications.

Graphical TOC Entry
Sustainable and renewable energy sources have become a long-standing aim in fulfilling the shortage of energy globally. Apart from solar energy, waste heat energy converted into electrical energy is a prominent source of renewable energy. To utilize this waste heat effectively, we need efficient thermoelectric materials. Advantageously, the thermoelectric generators are durable, robust, scalable, and compact and do not contain any moving parts. Note that, to have the maximum thermoelectric figure of merit ($zT$, see below), the material must have a large Seebeck coefficient ($\alpha$), along with high electrical conductivity ($\sigma$) and a low thermal conductivity ($\kappa$).

$$zT = \frac{\alpha^2 \sigma T}{\kappa}$$

However, the strong coupling between these parameters with a trade-off relationship is challenging to achieve a high $zT$ in a single system.

Halide-based perovskites have unveiled a paradigm shift in the quest for high-performance materials. This can be attributed to their compositional and structural diversity that enables a wide array of functional properties. More recently, halide perovskites have attracted attention for thermoelectric energy conversion due to their unique structural features and lattice dynamics. Yang et al. reported an ultralow thermal conductivity of 0.5 Wm$^{-1}$K$^{-1}$ in halide perovskite nanowires composed of CsPbI$_3$, CsPbBr$_3$ and CsSnI$_3$. Most of the reported thermoelectric materials, such as SnSe, PbTe, Cu$_2$Se, and BiCuSeO, have low intrinsic lattice thermal conductivity, similar in magnitude to that observed in halide perovskites. This exceptionally low thermal conductivity of halide perovskites, in conjunction with their high carrier mobility, makes them promising for thermoelectric investigations. However, unfortunately, these alluring materials suffer from lead toxicity and long-term instability. These drawbacks have motivated the scientific community to explore alternative perovskite compositions and structures.

One alternative class of materials is the inorganic lead-free double perovskites with the general formula $A_2BX_6$, commonly known as vacancy-ordered double perovskites. This defect-variant of halide perovskite is derived by doubling the $ABX_3$ unit cell along all three crystallographic axes.
and removing every alternate B-site cation, as illustrated in Figure 1. These perovskites provide new opportunities for non-toxic and stable replacements of Pb and Sn. Lately, vacancy-ordered double perovskites have been explored in thermoelectrics owing to their ultralow lattice thermal conductivity, which is attributed to their highly anharmonic lattice dynamics.\(^{14,16,31}\)

![Figure 1: Schematic of the relationship between ABX \(_3\) perovskite and A\(_2\)BX\(_6\) (vacancy-ordered) double perovskite.](image)

Motivated by this idea, in this Letter, we have studied the vacancy-ordered double perovskites A\(_2\)BX\(_6\) (A = Cs, B = Pt, Pd, Te, Sn, X = I) using state-of-the-art first-principles based methodologies under the framework of density functional theory (DFT) with suitable exchange-correlation (\(\epsilon_{xc}\)) functionals combined with many-body perturbative approaches (G\(_0\)W\(_0\)) and spin-orbit coupling (SOC). First, we have examined the structural, mechanical and thermodynamic stability of these materials. After that, we have studied the thermoelectric properties, where we find reasonably high \(zT\) values, calculated as a function of temperature \((T)\). Interestingly, we have observed the presence of anharmonic effects, which are quantified by computing both the harmonic and anharmonic energy contribution as a function of temperature in these vacancy-ordered double perovskites. In order to explore further, we have examined the stability and anharmonicity by computing the phonon bandstructures and electron localization function (ELF). The ELF further confirms the presence of anharmonicity in this class of systems. As a consequence, we find that the study of electron-phonon interaction is important. The electron-phonon interaction is well captured by calculating Fröhlich mesoscopic model\(^{32–34}\) to investigate the interaction of longitudinal optical phonon modes with the carriers that strongly influence the carrier mobility.
Cs$_2$BI$_6$ (B = Pt, Pd, Te, Sn) vacancy-ordered double perovskites have a face-centered cubic crystal structure with the space group $Fm\bar{3}m$ (no. 225). Each of the Cs atoms residing between the [BI$_6$] octahedra is surrounded by 12 I atoms. Moreover, each [BI$_6$] octahedra is located such that B atoms are at the corners and face-centered positions. The Cs atoms are situated at the 8c Wyckoff positions and (0.25, 0.25, 0.25) coordinates, B atoms at 4a Wyckoff positions and (0, 0, 0) coordinates, and I atoms at 24e Wyckoff positions and (x, 0, 0) coordinates, where the value of x is around 0.20. The optimized lattice parameters are listed in Table S1 of Supporting Information (SI).

Firstly, we have examined the stability of material as it is an essential factor in achieving a high-performance device applications. In order to predict the structural stability of the vacancy-ordered double perovskites, we have calculated the Goldschmidt tolerance factor ($t$) and octahedral factor ($\mu$). Recently, a new tolerance factor ($\tau$), proposed by Bartel et al. is also computed and compared for all the considered perovskites (see details in Sec. II in SI). The calculated values show that these perovskites are stable in cubic structures at room temperatures. Besides structural stability, we have also calculated the thermodynamic and mechanical stabilities. For thermodynamic stability, we have calculated the decomposition energy ($\Delta H_D$) as per the following equation:

$$\Delta H_D = E(Cs_2B_1I_6) - 2E(CsI) - E(B_1I_4)$$

where $E(Cs_2B_1I_6)$, $E(CsI)$ and $E(B_1I_4)$ are respectively the total DFT energies of Cs$_2$B$_1$I$_6$, CsI and B$_1$I$_4$. $\Delta H_D$ is calculated for all Cs$_2$B$_1$I$_6$ perovskites using Perdew-Burke-Ernzerhof (PBE) and Heyd–Scuseria–Ernzerhof (HSE06) $\epsilon_{xc}$ functionals. The values of $\Delta H_D$ are negative, indicating the thermodynamic stability of these perovskites. $\Delta H_D$ for all the considered perovskites are given in Sec. III of SI.

For the large-scale commercialization of a material, it is important to determine its mechanical properties. This leads to the calculation of elastic constants of the materials by using the finite strain theory. For cubic symmetry, three independent elastic constants viz., $C_{11}$, $C_{12}$ and $C_{44}$ are...
sufficient to explain the mechanical stability and related properties of the crystal. The corresponding mechanical stability criterion\textsuperscript{42,43} is given as follows:

\begin{equation}
C_{11} > 0, \ C_{44} > 0, \ C_{11} - C_{12} > 0, \ C_{11} + 2C_{12} > 0
\end{equation}

Using these elastic constants, we can calculate the bulk and shear moduli of all the perovskites. The Voigt bulk ($B_V$) and shear ($G_V$) moduli, Reuss bulk ($B_R$) and shear ($G_R$) moduli are calculated using the following relations:

\begin{align*}
B_V &= B_R = \frac{(C_{11} + 2C_{12})}{3} \\
G_V &= \frac{(C_{11} - C_{12} + 3C_{44})}{5} \\
G_R &= \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})}
\end{align*}

According to Voigt-Reuss-Hill approximations\textsuperscript{44}, Young’s modulus ($E$) and Poisson’s ratio ($\nu$) are obtained as:

\begin{align*}
B &= \frac{B_V + B_R}{2}, \quad G = \frac{G_V + G_R}{2} \\
E &= \frac{9BG}{3B + G} \\
\nu &= \frac{3B - 2G}{3B + G}
\end{align*}

The calculated elastic constants and moduli are given in Table 1. As we can see, the elastic constants satisfy the stability criteria, indicating the mechanical stability of these vacancy-ordered double perovskites. The fragility of these perovskites is studied in terms of Pugh’s and Poisson’s ratios. Pugh’s ratio ($B/G$) is the ratio between bulk modulus and shear modulus and is used to identify the ductile materials. If the ratio is found to be greater (or lower) than 1.75, the material is ductile (or brittle) (see Table 1 below). The calculated values of Pugh’s ratio show that the studied vacancy-ordered double perovskites are ductile. Similarly, Poisson’s ratio ($\nu$) can also distinguish
between ductile and brittle materials. For \( \nu \), the limiting value is 0.26. This is consistent with Pugh’s ratio. Also, we have calculated the elastic anisotropy \( (A) \) of these materials, given by the equation:

\[
A = \frac{2C_{44}}{C_{11} - C_{12}}
\]  

(10)

where \( A \) represents the elastic anisotropy coefficient. The value of \( A \) is equal to 1 for an isotropic crystal. The deviation from this value measures the degree of elastic anisotropy possessed by the crystal. According to the calculated values, all the considered double perovskites are anisotropic in nature.

Table 1: Calculated elastic constants \( C_{ij} \) (GPa), Bulk modulus \( B \) (GPa), Shear modulus \( G \) (GPa), Young’s modulus \( E \), Pugh’s ratio \( B/G \), Poisson’s ratio \( \nu \) and elastic anisotropy \( A \) of vacancy-ordered double perovskites.

| Compounds | \( C_{11} \) | \( C_{12} \) | \( C_{44} \) | \( B \) | \( G \) | \( E \) | \( B/G \) | \( \nu \) | \( A \) |
|-----------|----------------|----------------|----------------|----------|--------|--------|-----------|--------|--------|
| Cs\(_2\)PtI\(_6\) | 9.58 | 4.51 | 3.93 | 6.20 | 3.30 | 8.40 | 1.88 | 0.27 | 1.55 |
| Cs\(_2\)PdI\(_6\) | 16.64 | 8.98 | 7.36 | 11.53 | 5.66 | 11.39 | 2.04 | 0.29 | 1.92 |
| Cs\(_2\)TeI\(_6\) | 20.30 | 10.55 | 8.70 | 13.80 | 6.90 | 17.74 | 2.00 | 0.29 | 1.78 |
| Cs\(_2\)SnI\(_6\) | 14.36 | 8.20 | 6.65 | 10.25 | 4.88 | 12.63 | 2.10 | 0.29 | 2.16 |

After studying the stability, we have calculated the electronic band gaps (with and without SOC) of the vacancy-ordered double perovskites. Since simple local/semi-local \( \epsilon_{xc} \) functionals (viz. LDA, GGA) are unable to predict the band gaps correctly due to their incapability of capturing the electron’s self-interaction error, we have employed HSE06 \( \epsilon_{xc} \) and many-body perturbation theory \( (G_0W_0) \) to calculate the band gaps more accurately. The band gaps of Cs\(_2\)PtI\(_6\), Cs\(_2\)PdI\(_6\), Cs\(_2\)TeI\(_6\) and Cs\(_2\)SnI\(_6\) are 1.35, 1.43, 1.49 and 1.23 eV, respectively. All these perovskites have band gaps in visible region, which expands their scope for energy-harvesting applications. The values of band gaps agree well with the experimental values and are listed in Table 2. Also, the bandstructures, projected density of states (pDOS) and \( k \)-grid convergence data are provided for all perovskites in Sec. IV-VI of SI.

Next, we have calculated the thermoelectric properties of the perovskites using the BoltzTrap
Table 2: Band gaps of Cs$_2$BI$_6$ (B = Pt, Pd, Te, Sn) vacancy-ordered double perovskites using different $\varepsilon_{xc}$ functionals.

| Compounds  | PBE | PBE+SOC | HSE06 | HSE06+SOC | $G_0W_0$@PBE | $G_0W_0$@PBE+SOC | $G_0W_0$@HSE06+SOC |
|------------|-----|---------|-------|-----------|---------------|------------------|-------------------|
| Cs$_2$PtI$_6$ | 0.36 | 0.29 | 1.07 | 0.96 | 1.55 | 1.35$^{45}$ | - |
| Cs$_2$PdI$_6$ | 0.06 | 0.02 | 0.62 | 0.51 | 0.79 | 0.59 | 1.43$^{46}$ |
| Cs$_2$TeI$_6$ | 1.14 | 0.91 | 1.70 | 1.49$^{47}$ | 2.25 | 2.12 | - |
| Cs$_2$SnI$_6$ | 0.09 | 0.06 | 0.84 | 0.70 | 1.43 | 1.23$^{13}$ | - |

Code$^{48}$. Figure 2 (a-d) show the Seebeck coefficient ($\alpha$) as a function of chemical potential ($\mu$) for Cs$_2$BI$_6$ perovskites. $\alpha$ measures the induced thermoelectric voltage ($\Delta V$) in response to a temperature difference ($\Delta T$) across the material, as measured by the Seebeck effect and is given as $\alpha = \Delta V/\Delta T$. From the plot, we can see that at $\mu = 0$, the value of $\alpha$ is positive for Cs$_2$PtI$_6$ and Cs$_2$TeI$_6$ at various temperatures, indicating that these perovskites are p-type semiconductors. The maximum values of $\alpha$ for Cs$_2$PtI$_6$ and Cs$_2$TeI$_6$ are 710 and 190 $\mu$V/K, respectively, at 300 K. On the other hand, $\alpha$ is negative for Cs$_2$PdI$_6$ and Cs$_2$SnI$_6$, which indicates the n-type character in these perovskites$^{49}$. For Cs$_2$PtI$_6$ and Cs$_2$TeI$_6$, the maximum values of $\alpha$ are 148 and 290 $\mu$V/K, respectively, at 300 K. Also, we have observed that the value of $\alpha$ decreases with an increase in temperature for all the considered Cs$_2$BI$_6$ perovskites. Subsequently, to calculate the efficiency of material to convert heat into electrical energy, we have calculated the $zT$ as a function of temperature for the vacancy-ordered double perovskites. Figure 2 (e-h) show the $zT$ values at different temperatures for Cs$_2$BI$_6$ perovskites. The computed average $zT$ for Cs$_2$PtI$_6$, Cs$_2$PdI$_6$, Cs$_2$TeI$_6$ and Cs$_2$SnI$_6$ are 0.88, 0.85, 0.95 and 0.78, respectively, which make them promising for thermoelectric applications.

Low thermal conductivity is desirable for efficient thermoelectric materials, which in turn depends on lattice dynamics$^{50,51}$. Lattice dynamics play a pivotal role in governing materials properties such as thermal conductivity$^{52}$, ionic and electronic transport$^{53}$, optical emission$^{54}$, ferroelectricity$^{55}$ and superconductivity$^{56}$. Deviation from harmonic vibrational potential results in high amplitude anharmonic vibrations that introduce vibrational disorder in the system. This results in
significant phonon-phonon scattering, which leads to low thermal conductivities and better thermoelectric performance\textsuperscript{57–59}. To examine this deviation at high temperatures, we have calculated the harmonic ($U_h$) as well as anharmonic energy ($U_{ah}$) in vacancy-ordered double perovskites. $U_h$ is calculated under harmonic approximation for all perovskites. To quantify $U_{ah}$ in Cs$_2$BI$_6$ vacancy-ordered double perovskites, we have performed \textit{ab}MD calculations at different temperatures using Nose-Hoover thermostat\textsuperscript{60}. This data is then fed to a post-processing python package pyHMA\textsuperscript{61}, which determines the anharmonic energy (for details, see Sec. VII). Figure 3 (a-d) show the variation of $U_{ah}$ with temperature. As the temperature increases, we observe a deviation from harmonic potential leading to lattice anharmonicity.

The intimate connection between anharmonic lattice dynamics and functional properties motivates a fundamental understanding of anharmonicity in this class of materials. To further assess anharmonicity in our system, we have first examined the dynamical stability by plotting the phonon dispersion band structures of all Cs$_2$BI$_6$ perovskites using density functional perturbation theory (DFPT), as shown in Figure 4 (upper panel). For vacancy-ordered double perovskites, the structural
symmetry confirms 108 phonon modes as they contain 36 atoms per unit cell. Out of these 108 phonon modes, there are 3 acoustic modes, while the remaining modes are optical, characterized as low and high-frequency phonons, respectively. The absence of negative frequencies confirms the dynamical stability of these perovskites. After examining the phonon modes, we try to explore the interaction between atoms of these perovskites. The spatial distribution of the electron density around atom gives the measure of phonon anharmonicity. Therefore, we have computed the ELF to study materials bonding and anharmonicity (see Figure 4 (e-h)). The localization of electrons is estimated by a dimensionless ELF probability density ranging between 0 and 1. As we can see in Figure 4, I draws more charge because of its higher electronegativity in comparison to B atoms. Nevertheless, there is significant charge sharing among B-I bonds due to the small electronegativity difference, indicating the possibility of covalent bonding. On the other hand, no charge is shared between Cs and B/I atoms. However, physical interaction between Cs and [BI₆] octahedra results in nonspherical electron density around Cs and I atoms, which explains the origin of the phonon anharmonicity. This in turn increases the phonon scattering followed by suppression of the value of $\kappa^{58,59}$.

Anharmonic lattice dynamics give rise to stronger electron-phonon coupling in the material as electrons interact with lattice vibrations via the formation of polarons$^{62,63}$. To study these electron-phonon interactions, we have calculated the electron-phonon coupling strength using Fröhlich’s polaron model$^{34}$. The dimensionless Fröhlich electron-phonon coupling parameter ($\alpha$) measures
The electron-phonon coupling strength of the material and is given as:

$$\alpha = \frac{1}{4\pi\varepsilon_0} \frac{1}{2} \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_{\text{static}}} \right) \frac{e^2}{\hbar \omega_{\text{LO}}} \left( \frac{2m^* \omega_{\text{LO}}}{\hbar} \right)^{1/2}$$

(11)

The $\alpha$ depends on the material-specific properties, viz., optical ($\varepsilon_\infty$) and static ($\varepsilon_{\text{static}}$) dielectric constants, permittivity of free space ($\varepsilon_0$), the effective carrier mass ($m^*$) (for calculation of effective mass, see Sec. VIII in SI), and a characteristic longitudinal phonon angular frequency ($\omega_{\text{LO}}$). For a system having multiple phonon branches, an average LO frequency is calculated by considering all the infrared active optical phonon branches and taking a spectral average of them. The values of $\alpha$ for Cs$_2$Bi$_6$ perovskites are listed in Table 3 and follow the order: Cs$_2$PtI$_6$ > Cs$_2$PdI$_6$ > Cs$_2$TeI$_6$ > Cs$_2$SnI$_6$. The ELF and strong electron-phonon coupling validate the presence of anharmonicity in our considered perovskites. Also, the heavy atoms present in the system act as phonon rattlers and help suppress the lattice thermal conductivity effectively. This leads to their effective utilization in
high-performance thermoelectric device applications.

Table 3: Calculated polaron parameters for Cs$_2$BI$_6$ perovskites.

| Compounds    | $w_{LO}$ | $\varepsilon_e$ | $\varepsilon_\infty$ | $m_e^*$ | $\alpha_e$ |
|--------------|----------|-----------------|------------------------|---------|------------|
| Cs$_2$PtI$_6$ | 1.74     | 3.41            | 4.55                   | 0.49    | 2.24       |
| Cs$_2$PdI$_6$ | 1.62     | 2.80            | 3.30                   | 0.47    | 1.81       |
| Cs$_2$TeI$_6$ | 4.26     | 3.59            | 5.55                   | 0.40    | 1.73       |
| Cs$_2$SnI$_6$ | 3.52     | 2.67            | 3.46                   | 0.33    | 1.50       |

In summary, we have carried out an exhaustive study to investigate the structural, elastic and thermoelectric properties of A$_2$BX$_6$ (A = Cs, B = Pt, Pd, Te, Sn, X = I) vacancy-ordered perovskites under the framework of density functional theory. The Pugh’s and Poisson’s ratios (determined using Voigt-Reuss-Hill average approximation) show the ductile nature of the perovskites. Also, the negative formation energies and phonon band structures confirm the stability of these perovskites. The band gaps calculated using different $\varepsilon_{xc}$ functionals appear in visible region, which is advantageous for energy-harvesting properties. After that, we have calculated the Seebeck coefficient as a function of chemical potential. The $zT$ values for Cs$_2$PtI$_6$, Cs$_2$PdI$_6$, Cs$_2$TeI$_6$ and Cs$_2$SnI$_6$ are 0.88, 0.85, 0.95 and 0.78, respectively, which show that these perovskites are promising for thermoelectric applications. To examine the role of anharmonicity in these materials, we have plotted the ELF for these perovskites, which indicates the presence of lattice anharmonicity. Subsequently, we have calculated the harmonic and anharmonic energy in this class of materials. As a result of anharmonicity, these compounds have strong electron-phonon coupling and the strength of this coupling is quantified using Fröhlich’s polaron model. The phonon-phonon scattering owing to the presence of anharmonicity and heavy atoms acting as phonon rattlers results in low thermal conductivity and better thermoelectric properties.
Computational Methods

All the DFT calculations have been performed using the Vienna \textit{ab initio} simulation package (VASP)\textsuperscript{65,66}. The ion-electron interactions in all the elemental constituents are described using the projector augmented wave (PAW)\textsuperscript{67,68} method as implemented in VASP. The structural optimization is performed using generalized gradient approximation (PBE) and optB86 $\varepsilon_{xc}$ functional, relaxing all ions until Hellmann-Feynman forces are less than 0.001 eV/Å. The cutoff energy of 600 eV is used for the plane wave basis set such that the total energy calculations are converged within $10^{-5}$ eV. The $\Gamma$-centered $4 \times 4 \times 4$ $k$-grids are used to sample the Brillouin zones. The band gaps are calculated using hybrid $\varepsilon_{xc}$ functional (HSE06) and many-body perturbation theory. Note that the single-shot GW ($G_0W_0$\textsuperscript{69,70}) calculations have been performed on top of the orbitals obtained from PBE+SOC/HSE06+SOC $\varepsilon_{xc}$ functional [$G_0W_0@PBE+SOC/HSE06+SOC$]. The number of bands is set to four times the number of occupied bands. The polarizability calculations are performed on a grid of 50 frequency points. The effective mass is calculated by SUMO\textsuperscript{71} using a parabolic fitting of the band edges. The phonon calculations are performed for $2 \times 2 \times 2$ supercells using the PHONOPY package\textsuperscript{72,73}. The BoltzTrap Code, based on Boltzmann transport theory is used to evaluate thermoelectric properties. The self-consistent process described by Hellwarth is used to calculate the electron-phonon coupling strength\textsuperscript{33}. Static dielectric constants are calculated using density functional perturbation theory (DFPT) with a denser $k$-grid ($6 \times 6 \times 6$). To calculate the anharmonic energy, we have carried out \textit{ab initio} molecular dynamics (aiMD) simulation employing Nose-Hoover thermostat and pyHMA package.

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Supporting Information Available

See supplementary material for the details of optimized lattice parameters, Goldschmidt tolerance factor ($t$), octahedral factor ($\mu$) and new tolerance factor ($\tau$), decomposition energy ($\Delta H_D$), band-structures, projected density of states (pDOS) of Cs$_2$BI$_6$ perovskites, $k$-grid convergence, effective mass of Cs$_2$BI$_6$ perovskites and anharmonic energy of Cs$_2$BI$_6$ vacancy-ordered perovskites.

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Vacancy-ordered Double Perovskites $\text{A}_2\text{BX}_6$ ($\text{A} = \text{Cs}, \text{B} = \text{Pt, Pd, Te, Sn}, \text{X} = \text{I}$): An Emerging Class of Thermoelectric Materials

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I. Lattice parameters of Cs$_2$BI$_6$ (B = Pt, Pd, Te, Sn) vacancy-ordered double perovskites

II. Goldschmidt tolerance factor ($t$), octahedral factor ($\mu$) and new tolerance factor ($\tau$) of Cs$_2$BI$_6$ (B = Pt, Pd, Te, Sn) vacancy-ordered double perovskites

III. Decomposition energy ($\Delta H_D$) of Cs$_2$BI$_6$ (B = Pt, Pd, Te, Sn) vacancy-ordered double perovskites

IV. Bandstructures of Cs$_2$BI$_6$ (B = Pt, Pd, Te, Sn) vacancy-ordered double perovskites

V. Projected density of states (pDOS) of Cs$_2$BI$_6$ (B = Pt, Pd, Te, Sn) vacancy-ordered double perovskites

VI. $k$-grid convergence in Cs$_2$TeI$_6$ vacancy-ordered double perovskite

VII. Calculation of harmonic ($U_h$) and anharmonic energy ($U_{ah}$) in Cs$_2$BI$_6$ (B = Pt, Pd, Te, Sn) vacancy-ordered double perovskites

VIII. Effective mass calculation of Cs$_2$PtI$_6$ vacancy-ordered double perovskite
I. Lattice parameters of $\text{Cs}_2\text{BI}_6$ (B = Pt, Pd, Te, Sn) vacancy-ordered double perovskites

Table S1: Calculated lattice parameters (Å) of $\text{Cs}_2\text{BI}_6$ (B = Pt, Pd, Te, Sn) vacancy-ordered double perovskites using different $\epsilon_{xc}$ functionals.

| Compounds | Expt. | PBE   | PBE-vdW | optB86-vdW |
|-----------|-------|-------|---------|------------|
| $\text{Cs}_2\text{PtI}_6$ | 11.37 | 11.74 | 11.47   | 11.29      |
| $\text{Cs}_2\text{PdI}_6$ | 11.33 | 11.67 | 11.42   | 11.23      |
| $\text{Cs}_2\text{TeI}_6$ | 11.70 | 12.06 | 11.87   | 11.65      |
| $\text{Cs}_2\text{SnI}_6$ | 11.65 | 12.00 | 11.82   | 11.57      |

Table S1 shows the lattice parameters of vacancy-ordered double perovskites calculated using PBE and optB86 $\epsilon_{xc}$ functionals along with van der Waals (vdW) forces. The optB86-vdW $\epsilon_{xc}$ functional reproduces the lattice parameters of considered vacancy-ordered double perovskites close to experimental ones.
II. Goldschmidt tolerance factor ($t$), octahedral factor ($\mu$) and new tolerance factor ($\tau$) of Cs$_2$BI$_6$ (B = Pt, Pd, Te, Sn) vacancy-ordered double perovskites

Goldschmidt tolerance factor ($t$) and octahedral factor ($\mu$) are given as:

$$ t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} $$
$$ \mu = \frac{r_B}{r_X} $$

(1)

where $r_A$, $r_B$, and $r_X$ are the Shannon ionic radii$^1$ for A$^+$, B$^{4+}$ and X$^-$ ions, respectively. For stable cubic perovskites, the ranges of $t$ and $\mu$ are $0.8 \leq t \leq 1.0$ and $0.29 \leq \mu \leq 0.55$. The calculated values in Table S2 show that the considered perovskites are stable in cubic structures at room temperatures.

Recently, Bartel et al. have reported a new tolerance factor ($\tau$)$^2$ to predict the stability of a perovskite, which is given as:

$$ \tau = \frac{r_X}{r_B} - n_A \left( n_A - \frac{r_A/r_B}{\ln(r_A/r_B)} \right) $$

(2)

where $n_A$ is the oxidation state of A, $r_i$ is the ionic radius of ion $i$, $r_A < r_B$ by definition and $\tau < 4.18$ indicates perovskite (92% accuracy). Since the range of $\tau$ is calculated for ABX$_3$ and A$_2$BB$'$X$_6$ double perovskites, this may deviate for vacancy-ordered double perovskites (due to defects).
Table S2: Goldschmidt tolerance factor ($t$), octahedral factor ($\mu$) and new tolerance factor ($\tau$) of vacancy-ordered double perovskites

| Compounds     | $t$  | $\mu$ | $\tau$ |
|---------------|------|-------|--------|
| Cs$_2$PtI$_6$ | 0.28 | 1.00  | 5.25   |
| Cs$_2$PdI$_6$ | 0.28 | 1.01  | 5.31   |
| Cs$_2$TeI$_6$ | 0.44 | 0.91  | 4.19   |
| Cs$_2$SnI$_6$ | 0.31 | 0.99  | 4.90   |

III. Decomposition energy ($\Delta H_D$) of Cs$_2$BI$_6$ ($B = $ Pt, Pd, Te, Sn) vacancy-ordered double perovskites

Reactions for decomposition of Cs$_2$BI$_6$ vacancy-ordered double perovskites:

 Cs$_2$PtI$_6$ $\rightarrow$ 2CsI + PtI$_4$
 Cs$_2$PdI$_6$ $\rightarrow$ CsI$_3$ + PdI$_2$ + CsI
 Cs$_2$TeI$_6$ $\rightarrow$ 2CsI + TeI$_4$
 Cs$_2$SnI$_6$ $\rightarrow$ 2CsI + SnI$_4$

The values of $\Delta H_D$ are listed in Table S3. The negative values confirm the thermodynamic stability of these vacancy-ordered double perovskites (see Figure S1).

Table S3: $\Delta H_D$ of Cs$_2$BI$_6$ perovskites using PBE and HSE06 $\epsilon_{xc}$ functionals

| Compounds     | $\Delta H_D$ (eV/atom) (PBE) | $\Delta H_D$ (eV/atom) (HSE06) |
|---------------|------------------------------|--------------------------------|
| Cs$_2$PtI$_6$ | -0.60                        | -0.74                          |
| Cs$_2$PdI$_6$ | -0.02                        | -0.13                          |
| Cs$_2$TeI$_6$ | -1.07                        | -1.14                          |
| Cs$_2$SnI$_6$ | -0.34                        | -0.42                          |
Figure S1: $\Delta H_D$ of (a) Cs$_2$PtI$_6$ (b) Cs$_2$PdI$_6$ (c) Cs$_2$TeI$_6$ and (d) Cs$_2$SnI$_6$ vacancy-ordered double perovskites.

IV. Bandstructures of Cs$_2$BI$_6$ ($B = \text{Pt, Pd, Te, Sn}$) vacancy-ordered double perovskites

Figure S2: Bandstructures of (a) Cs$_2$PtI$_6$ (b) Cs$_2$PdI$_6$ (c) Cs$_2$TeI$_6$ and (d) Cs$_2$SnI$_6$ vacancy-ordered double perovskites, calculated using HSE06+SOC $\epsilon_{xc}$ functional.

The bandstructures for Cs$_2$PtI$_6$, Cs$_2$PdI$_6$, Cs$_2$TeI$_6$ and Cs$_2$SnI$_6$ are calculated using HSE06+SOC $\epsilon_{xc}$ functional (see Figure S2) and the band gaps of these perovskites are 0.96, 0.79, 2.25 and 1.43 eV, respectively.
V. Projected density of states (pDOS) of Cs$_2$BI$_6$ (B = Pt, Pd, Te, Sn) vacancy-ordered double perovskites

Figure S3: Projected density of states (pDOS) of (a) Cs$_2$PtI$_6$ (b) Cs$_2$PdI$_6$ (c) Cs$_2$TeI$_6$ and (d) Cs$_2$SnI$_6$ vacancy-ordered double perovskites, calculated using HSE06+SOC $\epsilon_{xc}$ functional.

Figure S3 shows the pDOS of all four vacancy-ordered double perovskites. The valence band maxima (VBM) of these perovskites are mostly dominated by I-p orbitals while conduction band minima (CBm) are contributed by I-p orbitals along with Pt-d, Pd-d, Te-p and Sn-s orbitals in Cs$_2$PtI$_6$, Cs$_2$PdI$_6$, Cs$_2$TeI$_6$ and Cs$_2$SnI$_6$, respectively. Also, the VBM is composed of Pt-d, Pd-d and Te-s orbitals in Cs$_2$PtI$_6$, Cs$_2$PdI$_6$ and Cs$_2$TeI$_6$, respectively. The CBm is also composed of Pt-d, Pd-d, Te-p and Sn-p orbitals in Cs$_2$PtI$_6$, Cs$_2$PdI$_6$, Cs$_2$TeI$_6$ and Cs$_2$SnI$_6$, respectively. There is a strong hybridization of Te-p and I-p orbitals in Cs$_2$TeI$_6$ and Sn-s and I-p orbitals in Cs$_2$SnI$_6$. 

S7
VI. $k$-grid convergence in $\text{Cs}_2\text{TeI}_6$ vacancy-ordered double perovskite

Figure S4: Imaginary (Im($\varepsilon$)) and real (Re($\varepsilon$)) part of dielectric function for $\text{Cs}_2\text{TeI}_6$ vacancy-ordered double perovskite using PBE $\epsilon_{xc}$ functional.

Fig. S4 (a) and (b) show the variation of imaginary (Im($\varepsilon$)) and real part (Re($\varepsilon$)) of dielectric function for $\text{Cs}_2\text{TeI}_6$ vacancy-ordered double perovskite. On increasing $k$-grid, no shift is observed in first peak position of Im($\varepsilon$) part of dielectric function. Hence, $4 \times 4 \times 4$ $k$-grid is sufficient to compute quasi particle ($G_0W_0$) band gap.
VII. Calculation of harmonic ($U_h$) and anharmonic energies ($U_{ah}$) in Cs$_2$BI$_6$ (B = Pt, Pd, Te, Sn) vacancy-ordered double perovskites

Harmonic energy ($U_h$) is calculated as per the following equation:

$$U_h = \sum_i \frac{h\nu_i}{2} + \sum_i k_B T \ln\left[1 - \exp\left(\frac{h\nu_i}{k_B T}\right)\right]$$

(3)

where $k_B$, $h$, and $T$ are respectively the Boltzmann constant, Planck constant, and temperature. $\nu_i$ represent frequencies of vibration which we get from vibration calculation in VASP.

To calculate the anharmonic energy, we have performed aiMD calculations at 250 K, 500 K, 750 K, 1000 K, 1250 K, 1500 K, 1750 K and 2000 K temperatures using Nose-Hoover thermostat with time and time-step being 8 ps and 1 fs, respectively. This data is then supplied to a post-processing python package pyHMA,$^3$ which determines the anharmonic energy according to the relation:

$$U_{ah} = \langle U + \frac{1}{2} \mathbf{F} \cdot \Delta \mathbf{r} \rangle - U_{lat}$$

(4)

where the $\mathbf{F}$ vector represents the forces on all atoms, and $\Delta \mathbf{r}$ are the displacements of each atom from its lattice (equilibrium) site. The pyHMA package reads MD data from output file (vasprun.xml) to compute anharmonic energy. The package can be downloaded from the development version on GitHub.
VIII. Effective mass calculation of Cs\(_2\)PtI\(_6\) vacancy-ordered double perovskite

Calculation of effective masses using SUMO package.

**Electron effective masses:**

\[ m_e : 0.491 \mid \text{band 284} \mid [0.00, 0.00, 0.00] \, (\Gamma) \rightarrow [0.50, 0.50, 0.50] \, (L) \]

\[ m_e : 0.489 \mid \text{band 284} \mid [0.00, 0.00, 0.00] \, (\Gamma) \rightarrow [0.50, 0.00, 0.50] \, (X) \]

\[ m_e : 0.491 \mid \text{band 285} \mid [0.00, 0.00, 0.00] \, (\Gamma) \rightarrow [0.50, 0.50, 0.50] \, (L) \]

\[ m_e : 0.489 \mid \text{band 285} \mid [0.00, 0.00, 0.00] \, (\Gamma) \rightarrow [0.50, 0.00, 0.50] \, (X) \]

\[ m_e : 0.491 \mid \text{band 286} \mid [0.00, 0.00, 0.00] \, (\Gamma) \rightarrow [0.50, 0.50, 0.50] \, (L) \]

\[ m_e : 0.489 \mid \text{band 286} \mid [0.00, 0.00, 0.00] \, (\Gamma) \rightarrow [0.50, 0.00, 0.50] \, (X) \]

To calculate the average electron mass at \( \Gamma \)-point, we have taken the average of masses along \( \Gamma \rightarrow L \) and \( \Gamma \rightarrow X \) directions.

Average effective electron mass = 0.49 \( m_0 \)
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