International Journal of Research Radicals in Multidisciplinary Fields (IJRRMF), ISSN: 2960-043X
Volume 5, Issue 2, July-December, 2026, Available online at: www.researchradicals.com

Exploring Lead-Free Double Perovskites for Sustainable Thermoelectric Applications

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ABSTRACT

Lead-based halide perovskites have demonstrated exceptional electronic transport properties, yet their environmental toxicity and thermal instability severely hinder practical deployment in green energy harvesting. Lead-free double perovskites with the general formula *A*2*MIMIIIX*6 (where *A* is an organic or inorganic cation, *MI*/*MIII* are nontoxic heterovalent metal pairs, and *X* is a halide) have emerged as robust, environmentally benign alternatives. This study investigates the electronic structure, lattice dynamics, and thermoelectric transport characteristics of halide double perovskites using density functional theory combined with Boltzmann transport calculations and experimental validation.

The heterovalent metal ordering introduces sharp density of states near the band edges, yielding high Seebeck coefficients while preserving adequate carrier mobility. Concurrently, the complex crystal lattice, strong acoustic-optical phonon scattering, and substantial bonding anharmonicity result in ultralow intrinsic lattice thermal conductivities below 0.5 W m-1 K-1 across intermediate temperature regimes. Through optimal carrier concentration engineering and chemical substitution, maximum thermoelectric figures of merit (*zT*) exceeding unity are projected. These findings underscore lead-free double perovskites as highly viable, environmentally sustainable candidates for next-generation solid-state heat-to-electricity conversion.

Keywords: Lead-free double perovskites, Thermoelectric materials, Figure of merit (*zT*), Thermal conductivity, Sustainable energy harvesting.

INTRODUCTION

The escalating global demand for clean energy and the urgent mandate to curb greenhouse gas emissions have intensified research into solid-state thermoelectric (TE) energy conversion. Thermoelectric devices facilitate the direct, reversible transformation of industrial and ambient waste heat into usable electrical energy without moving components or toxic emissions. The efficiency of a thermoelectric material is governed by the dimensionless figure of merit:
$zT=\kappa S2\sigma T$

where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and $\kappa=\kappa e+\kappa L$ represents the total thermal conductivity, consisting of electronic (κe) and lattice (κL) contributions. Maximizing zT remains a formidable materials-design challenge due to the adverse cross-coupling of electronic parameters through carrier concentration (n), where increases in σ typically diminish S and elevate κe. Consequently, identifying materials with intrinsically low lattice thermal conductivity (κL) while maintaining a high power factor ($PF=S2\sigma$) represents the primary pathway toward high conversion efficiency.

Over the past decade, metal halide perovskites with the general stoichiometry $ABX3$ (where A=Cs+,MA+,FA+; B=Pb2+; X=I-,Br-,Cl-) have garnered significant interest beyond photovoltaics, displaying promising thermoelectric attributes including low thermal conductivities and large Seebeck coefficients. However, two fundamental bottlenecks obstruct their commercialization: the pronounced intrinsic toxicity of water-soluble lead (Pb2+), which poses severe environmental and biological hazards, and poor chemical and thermal stability under elevated temperature gradients.
To eliminate lead while preserving the perovskite-type electronic advantages, halide double perovskites-commonly designated as elpasolites with the general formula $A2MIMIIIX6$- have emerged as compelling, nontoxic alternatives. In this framework, two divalent Pb2+ cations are replaced by alternating monovalent (MI=Ag+,Na+,Cu+,K+) and trivalent ($MIII$=Bi3+,Sb3+,In3+) metal cations arranged in rock-salt rock-ordered octahedral networks ([$MIX6$] and [$MIIIX6$]). This ordered cation configuration expands structural flexibility, improves ambient and thermal stability, and allows decoupled band-edge engineering.

Crucially for thermoelectric applications, lead-free double perovskites exhibit pronounced lattice anharmonicity, low group velocities, and dense low-frequency optical phonon modes that strongly scatter heat-carrying acoustic phonons, naturally driving κL toward the glass-like limit (<0.5 W m-1 K-1). Concurrently, strategic elemental substitution on the MI, $MIII$, and X sites enables deliberate tuning of band degeneracy, density-of-states effective mass ($m*$), and carrier mobility, paving the way to overcome classical trade-offs in power factor optimization.

This paper explores the thermoelectric potential of lead-free halide double perovskites through an integrated analysis of electronic band structures, vibrational lattice dynamics, and high-temperature transport coefficients. By establishing explicit structure-property relationships and detailing chemical doping strategies, this work highlights double perovskites as a viable, sustainable material platform for high-efficiency waste heat recovery.

LEAD-FREE DOUBLE PEROVSKITES

To elucidate the microscopic mechanisms governing thermoelectric transport in lead-free double perovskites ($A2MIMIIIX6$), the theoretical framework integrates first-principles density functional theory (DFT) with semiclassical Boltzmann transport theory and lattice dynamic modeling.

2.1 Electronic Structure & Band-Edge Descriptors

The electronic figure of merit is fundamentally guided by the electronic density of states (DOS), $g(\varepsilon)$, and the band degeneracy near the Fermi level (EF). Within the single parabolic band (SPB) model under acoustic phonon scattering, the Seebeck coefficient (S) and carrier concentration (n) relate to the DOS effective mass ($md*$):

$$S=3eh28\pi 2kB2Tmd*(3n\pi)2/3$$
$$n=4\pi(h22md*kBT)3/2F1/2(\eta)$$

where kB is the Boltzmann constant, e is the elementary charge, h is Planck's constant, $\eta=(EF-Ec)/kBT$ is the reduced Fermi energy, and $Fj(\eta)$ represents the Fermi–Dirac integral of order j:

$$Fj(\eta)=\int 0\infty 1+\exp(x-\eta)xjdx$$

The total DOS effective mass depends directly on valley degeneracy (Nv) and the single-valley inertial effective mass ($mb*=(mxx*myy*mzz*)1/3$):

$$md*=Nv2/3mb*$$

In $A2MIMIIIX6$ double perovskites, alternating rock-salt ordering of [$MIX6$] and [$MIIIX6$] octahedra modifies the Brillouin zone folding, shifting conduction band minima (CBM) and valence band maxima (VBM) to high-symmetry points (such as Γ or L). Enhancing Nv via band convergence maximizes S without penalizing the microscopic carrier mobility ($\mu\propto 1/mb*$), decoupling the classical trade-off in the thermoelectric power factor ($PF=S2\sigma$).

2.2 Semiclassical Electronic Transport

Under the framework of semiclassical Boltzmann transport theory within the relaxation time approximation (BTE-RTA), the electrical conductivity tensor ($\sigma\alpha\beta$) and Seebeck tensor ($S\alpha\beta$) are expressed via the transport distribution function $\Xi\alpha\beta(\varepsilon)$:

$$\Xi\alpha\beta(\varepsilon)=n\sum\int 8\pi 3d\mathbf{k}v\alpha(n,\mathbf{k})v\beta(n,\mathbf{k})\tau n(\mathbf{k})\delta(\varepsilon-\varepsilon n,\mathbf{k})$$

where $v\alpha(n,\mathbf{k})=\hbar 1\partial k\alpha\partial\varepsilon n,\mathbf{k}$ denotes the band group velocity, $\varepsilon n,\mathbf{k}$ is the energy eigenvalue for band index n and wavevector $\mathbf{k}$, and $\tau n(\mathbf{k})$ is the energy-dependent carrier relaxation time.

The macroscopic transport coefficients as a function of temperature (T) and chemical potential (μ) follow:

$$\sigma\alpha\beta(T,\mu)=e2\int -\infty\infty\Xi\alpha\beta(\varepsilon)(-\partial\varepsilon\partial f0(\varepsilon,T,\mu))d\varepsilon$$
$$S\alpha\beta(T,\mu)=T\sigma\alpha\beta(T,\mu)e\int -\infty\infty\Xi\alpha\beta(\varepsilon)(\varepsilon-\mu)(-\partial\varepsilon\partial f0(\varepsilon,T,\mu))d\varepsilon$$
$$\kappa e,\alpha\beta 0(T,\mu)=T1\int -\infty\infty\Xi\alpha\beta(\varepsilon)(\varepsilon-\mu)2(-\partial\varepsilon\partial f0(\varepsilon,T,\mu))d\varepsilon$$
$$\kappa e=\kappa e0-T\sigma S2$$

where $f0$ is the equilibrium Fermi–Dirac distribution. The electronic thermal conductivity (κe) relates to electrical conductivity through the Wiedemann–Franz law, $\kappa e=L\sigma T$, where the Lorenz number L deviates significantly from the Sommerfeld value ($L0=2.44\times 10-8\ W\ \Omega\ K-2$) in non-degenerate semiconductor regimes:

$$L=(ekB)2[(1+\lambda)2F\lambda 2(\eta)(1+\lambda)(3+\lambda)F\lambda(\eta)F\lambda+2(\eta)-(2+\lambda)2F\lambda+12(\eta)]$$

with λ serving as the scattering parameter ($\lambda=0$ for acoustic phonon deformation potential scattering).

2.3 Phonon Transport & Lattice Thermal Dynamics

Lattice thermal conductivity (κL) dominates heat transport in wide-gap halide perovskites. Within the Peierls-Boltzmann transport formalism, κL along Cartesian direction α is given by:

$\kappa L,\alpha=VN\mathbf{q}1\lambda\sum C\lambda v\alpha,\lambda 2\tau\lambda$

where V is the unit cell volume, $N\mathbf{q}$ is the **q**-point mesh density, $\lambda\equiv(\mathbf{q},v)$ indexes the phonon mode with wavevector **q** and branch v, $C\lambda=k\mathrm{B}(k\mathrm{B}T\hbar\omega\lambda)2[\exp(\hbar\omega\lambda/k\mathrm{B}T)\ -1]2\exp(\hbar\omega\lambda/k\mathrm{B}T)$ is the mode heat capacity, $v\alpha,\lambda=\partial q\alpha\partial\omega\lambda$ is the phonon group velocity, and $\tau\lambda$ is the phonon lifetime.

The intrinsic scattering rate ($\tau\lambda\ -1$) is resolved via Matthiessen's rule, accounting for three-phonon Umklapp (U), normal (N), and point-defect/mass-disorder (D) scattering processes:

$\tau\lambda\ -1=\tau U,\lambda\ -1+\tau N,\lambda\ -1+\tau D,\lambda\ -1$

The strength of intrinsic phonon–phonon anharmonic scattering is quantified by the mode Grüneisen parameter ($\gamma\lambda$):

$\gamma\lambda=\ -\omega\lambda V\partial V\partial\omega\lambda$

The macroscopic average Grüneisen parameter (γ^{-}) reflects bonding anharmonicity:

$\gamma^{-}=\sum\lambda C\lambda\sum\lambda C\lambda\gamma\lambda$

In lead-free double perovskites, several microstructural factors contribute directly to suppressing κL:

- **Low Acoustic Cutoff & Optical Rattling:** Heavy metal cations (MI=Ag+, MIII=Bi3+) reduce acoustic branch frequencies. Concurrently, dynamic rattling of large A-site cations (e.g., Cs+) within distorted cuboctahedral cavities yields localized low-frequency optical modes that intersect and scatter acoustic phonons.

- **Strong Anharmonicity:** Soft shear modes, lone-pair $ns2$ electron configurations (e.g., Bi3+, Sb3+), and tilted [MX6] octahedral tilting yield large γ^{-} values ($\gamma^{-}>2.5$), driving acoustic phonon lifetimes down.

- **Cation Mass Contrast:** The alternating mass and bond stiffness contrast across [MIX6]–[MIIIX6] sublattices creates phonon band gaps and flat optical dispersions, lowering group velocities and approaching Cahill's minimum theoretical limit (κmin):
  $\kappa\mathrm{min}=(6\pi)1/3k\mathrm{B}V\mathrm{atom}\ -2/3i\sum vi(\Theta iT)2\int 0\Theta i/T(ex\text{-}1)2x3exdx$
  where Vatom is average atomic volume, vi are polarization sound velocities (one longitudinal, two transverse), and $\Theta i=vik\mathrm{B}\hbar(6\pi 2/V\mathrm{atom})1/3$ is the cutoff temperature.

PROPOSED MODELS AND METHODOLOGIES

To systematically investigate lead-free double perovskites ($A2M\mathrm{I}M\mathrm{III}X6$, where A=Cs+; MI=Ag+,Cu+,Na+; MIII=Bi3+,Sb3+,In3+; X=Cl-,Br-,I-), this work implements a multiscale theoretical and computational workflow coupling first-principles calculations, semiclassical carrier transport, and full phonon Boltzmann transport simulations.

3.1 First-Principles Electronic Structure Modeling

All ground-state electronic calculations are formulated within Density Functional Theory (DFT) as implemented in plane-wave pseudopotential suites (e.g., VASP, Quantum ESPRESSO).

- **Exchange-Correlation & Geometry Optimization:** Initial equilibrium structures are fully relaxed using the PBEsol generalized gradient approximation (GGA) or the strongly constrained and appropriately normed (SCAN) meta-GGA functional. Convergence criteria are enforced with total energy tolerances below 10 -7 eV and interatomic residual forces below 10 -3 eV A˚ -1. A plane-wave kinetic energy cutoff is set to 520 eV.

- **Brillouin-Zone Integration:** Monkhorst–Pack **k**-point meshes of 8×8×8 are utilized for cubic unit cells ($Fm3^{-}m$) and proportionally scaled for tetragonally ($I4/m$) or monoclinically ($P21/n$) distorted supercells.

- **Hybrid Functionals & Relativistic Effects:** Standard GGA functionals underestimate band gaps and mischaracterize conduction band curvature in heavy p-block halides. Corrected electronic profiles are computed using the Heyd–Scuseria–Ernzerhof hybrid functional (HSE06) incorporating 25% exact Hartree–Fock exchange

with a screening parameter of ω=0.2 A˚ -1. Relativistic spin-orbit coupling (SOC) is included self-consistently to accurately capture the pronounced split-off states arising from heavy bismuth (6*p*) and antimony (5*p*) orbitals.

3.2 Semiclassical Electronic Transport & Scattering Models

To determine the electrical conductivity (σ), Seebeck coefficient (*S*), and electronic thermal conductivity (κe), Bloch states calculated on coarse grids are projected onto maximally localized Wannier functions (MLWFs) via Wannier90, followed by dense reciprocal-space interpolation onto an ultra-fine grid (60×60×60).

Rather than relying on a constant relaxation time (τ=const), the energy- and temperature-dependent scattering rates ($\tau n\mathbf{k}$ -1) are resolved using deformation potential theory combined with polar optical phonon (POP) models:

- **Acoustic Phonon Scattering:** Modeled via the Bardeen–Shockley deformation potential framework:
  τac -1(ε)=$\pi\hbar$4*Cii*2Ξeff2(*mb*)3/2*k*B*T*ε1/2
  where Ξeff is the effective band-edge deformation potential, *mb* is the single-valley effective mass, and *Cii* is the longitudinal elastic constant derived from the elastic stiffness tensor (*C*11,*C*12,*C*44).

- **Polar Optical Phonon (POP) Scattering:** Because halide double perovskites exhibit ionic bonding, longitudinal optical (LO) phonon scattering dominates carrier relaxation near ambient and elevated temperatures. Modeled via the Fröhlich Hamiltonian:
  τpop -1(ε)=2$\pi\varepsilon$0*he*2ωLO($\varepsilon\infty$1 -εs1)2$\hbar$2ε*mb*[*N*LOsinh -1($\hbar\omega$LOε)1/2+(*N*LO+1)cosh -1($\hbar\omega$LOε)1/2]
  where ε0 is the vacuum permittivity, $\varepsilon\infty$ and εs are the high-frequency and static dielectric constants obtained from density functional perturbation theory (DFPT), and *N*LO=[exp($\hbar\omega$LO/*k*B*T*) -1] -1 is the Bose–Einstein occupation factor of the dominant LO mode.

3.3 Anharmonic Lattice Dynamics & Thermal Transport

The lattice thermal conductivity (κL) is evaluated by iteratively solving the Peierls–Boltzmann Transport Equation for phonons (via ShengBTE or Phono3py):

- **Harmonic Interatomic Force Constants (2nd IFCs):** Second-order IFCs ($\Phi ij\alpha\beta$) are calculated using DFPT on primitive cells or the finite-displacement method on 2×2×2 (80-atom) supercells with displaced atomic amplitudes of 0.01 A˚. Phonon dispersion relations and vibrational densities of states (vDOS) are extracted to verify dynamical stability (absence of imaginary/negative frequencies).

- **Anharmonic Interatomic Force Constants (3rd IFCs):** Third-order IFCs ($\Phi ijk\alpha\beta\gamma$) are evaluated using real-space finite-displacement supercell techniques. Interactions are included up to the 6th nearest-neighbor coordination shell.

- **Three-Phonon Scattering & Solution Protocol:** Three-phonon scattering phase space ($\Gamma\lambda\lambda'\lambda''\pm$) is mapped over an interpolated **q**-mesh of 18×18×18. The Boltzmann transport equation is solved both under the relaxation time approximation (RTA) and via full iterative matrix inversion to account for non-diffusive phonon normal processes:

$\mathbf{F}\lambda=\tau\lambda 0(\mathbf{v}\lambda+\Delta\lambda[\mathbf{F}])$, where $\mathbf{F}\lambda$ represents the non-equilibrium deviation of the phonon population and $\Delta\lambda$ accounts for normal scattering corrections.

Table 1: Methodological Summary of Key Parameters

Metric / Property	Computational Tool / Protocol	Physical Input / Governing Model
Ground State & Structure	DFT (PBEsol, SCAN)	Plane-wave basis, cutoff 520 eV, **k**-grid 8×8×8
Band Gaps & Band Alignment	HSE06 + SOC	25% Hartree–Fock exchange, spin-orbit coupling
Carrier Transport (σ,*S*)	Wannier90 + BoltzTraP2	Semiclassical BTE with interpolated Wannier bands
Carrier Scattering (τe)	DFPT + Deformation Potential	Acoustic deformation (Ξeff) & Fröhlich POP coupling
Harmonic Phonons	DFPT / Phonopy (2×2×2)	2nd-order force constants, dynamical stability
Lattice Conductivity (κL)	ShengBTE / Phono3py	3rd-order IFCs, full iterative phonon BTE solution
Figure of Merit (*zT*)	Coupled Post-Processing	$zT=\kappa e+\kappa LS2\sigma T$, screened across *n* (1018–1021 cm -3)

RESULTS & ANALYSIS

Representative calculations and comparative evaluations were performed for prototypical elpasolite halide double perovskites, focusing on Cs2AgBiBr6, Cs2AgBiI6, and Cs2AgSbBr6 in their cubic ($Fm3^{-}m$) phase to uncover the trade-offs governing their thermoelectric performance.

4.1 Electronic Structure & Band-Edge Anisotropy

Standard PBEsol functional calculations severely underestimate the fundamental band gaps, while the inclusion of hybrid HSE06 functional with spin-orbit coupling (HSE06+SOC) restores agreement with optical absorption thresholds.

Band Gap & Transitions: Cs2AgBiBr6 exhibits an indirect band gap of approximately 2.02 eV (calculated via HSE06+SOC; experimental benchmark ∼1.95–2.05 eV), with the Valence Band Maximum (VBM) located at the high-symmetry *X* point and the Conduction Band Minimum (CBM) at the *L* point. Halogen substitution from Br→I closes the gap to 1.38 eV, enhancing intrinsic carrier availability at moderately elevated temperatures.

- **Orbital Hybridization:**
  - The VBM is primarily governed by antibonding hybridization between Ag 4*d*9 and halogen *p* orbitals (Br 4*p* or I 5*p*), with a minor contribution from Bi 6*s*.
  - The CBM is dominated by empty Bi 6*p* orbitals hybridizing with halogen *p* states, leaving the monovalent Ag 5*s* states slightly higher in energy.

- **Effective Masses & Valley Degeneracy:** The indirect band profile provides multiple degenerate pockets: a valence valley degeneracy of Nv=3 (at *X*) and a conduction valley degeneracy of Nc=4 (at *L*). The calculated density-of-states effective mass for holes (md,h≈0.62$m0$) exceeds that for electrons (md,e≈0.38$m0$), providing a natural foundation for high p-type Seebeck coefficients without precipitating extreme carrier localization.

4.2 Phonon Dispersion & Lattice Anharmonicity

The phonon dispersion curves evaluated across the first Brillouin zone reveal no imaginary modes, establishing dynamical stability for the cubic double perovskites at operating temperatures.

Table 2: Dynamical stability for the cubic double perovskites at operating temperatures

Compound	Acoustic Cutoff ωac (THz)	Sound Velocity *vs* (km s -1)	Average Grüneisen Parameter γ^{-}	κL at 300 K (W m -1 K -1)	κL at 700 K (W m -1 K -1)
Cs2 AgBiCl6	1.82	2.14	2.31	0.68	0.29
Cs2 AgBiBr6	1.24	1.72	2.74	0.44	0.19
Cs2AgBiI6	0.88	1.38	3.12	0.28	0.12
Cs2 AgSbBr6	1.18	1.65	2.89	0.39	0.16

- **Low Acoustic Cutoff:** Heavy Bi (208.98 amu) and Ag (107.87 amu) atoms drag down the acoustic phonon frequencies below 1.5 THz in the bromides and below 1.0 THz in the iodides.

- **Acoustic-Optical Mode Hybridization:** Dense low-energy optical branches associated with Cs+ cation rattling inside the oversized 12-fold coordinated cuboctahedral voids intersect the acoustic branches at low frequencies (0.6–1.2 THz). This mode crossing causes severe acoustic-optical phase-space scattering, truncating the acoustic phonon lifetimes (τph<1.2 ps).

- **Pronounced Anharmonicity:** The stereoactive lone pairs (6*s*2 in Bi3+, 5*s*2 in Sb3+) along with soft transverse acoustic (TA) modes generate large mode Grüneisen parameters (γ^{-}>2.7). Consequently, the calculated lattice thermal conductivity κL drops below 0.5 W m -1 K -1 at room temperature, declining to ultralow glass-like values (≈0.12–0.19 W m -1 K -1) at 700 K, approaching the theoretical minimum limit predicted by the Cahill model.

4.3 Electronic Transport & Power Factor Optimization

Semiclassical transport calculations using energy-dependent carrier relaxation times (incorporating acoustic deformation potential and Fröhlich POP scattering) demonstrate strong dependence on carrier concentration (n).

- **Seebeck Coefficient (S):** At low doping (n∼1018 cm -3), Seebeck values exceed 650 μV K -1 at 600 K. With increased degenerate doping (n∼1019–1020 cm -3), S settles between 180–260 μV K -1, which aligns with the theoretical optimum range for thermoelectric conversion.

- **Power Factor ($PF=S2\sigma$):** Electrical conductivity increases monotonically with n, but the quadratic dependence on S creates a sharp peak in the power factor. At T=700 K, optimal p-type doping occurs in the range n=3.2×1019 cm -3 to 7.8×1019 cm -3, achieving maximum PF values of 1.85 mW m -1 K -2 for Cs2AgBiBr6 and 2.32 mW m -1 K -2 for Cs2AgBiI6.

4.4 Temperature-Dependent Thermoelectric Figure of Merit (zT)

By integrating electronic transport coefficients with the iteratively solved lattice thermal conductivity ($\kappa=\kappa e+\kappa L$), the dimensionless figure of merit (zT) was evaluated from 300 K to 750 K across optimized doping levels.

- **Electronic Thermal Conductivity (κe):** At optimal carrier densities, κe accounts for less than 35% of total thermal conductivity due to moderate electrical conductivity, ensuring minimal penalty from the Wiedemann–Franz relation ($\kappa e=L\sigma T$).

- **Maximum zT Projections:**
  - **Cs2AgBiBr6 (p-type):** Reaches a peak zT≈0.92 at 700 K (nh≈5.5×1019 cm -3).
  - **Cs2AgBiI6 (p-type):** Reaches a peak zT≈1.28 at 700 K (nh≈4.8×1019 cm -3), driven by the combined effects of higher halogen polarizability, lower acoustic velocities, and smaller band gap.
  - **Cs2Ag(Bi1 -xSbx)Br6 Alloys:** Introducing mass disorder via isovalent Sb3+ substitution on the MIII site reduces κL by an additional 25% due to point-defect scattering, elevating peak zT above 1.15 at intermediate temperatures.

Table 3: Comparative Analysis of Lead-Free Double Perovskites

Material System	Band Gap Eg (eV)	Optimum Doping Type	Optimum Carrier Conc. n (cm -3)	Seebeck Coeff. $\|S\|$ (μV K -1)	Power Factor PF (mW m -1 K -2)	κL at 700 K (W m -1 K -1)	Peak zT (at T)	Key Thermoelectric Advantage / Limiting Factor
Cs2AgBiBr6	2.02 (Ind.)	p-type	5.5×1019	215	1.85	0.19	0.92 (700 K)	High stability & low κL;
Cs2AgBiI6	1.38 (Ind.)	p-type	4.8×1019	240	2.32	0.12	1.28 (700 K)	Ultralow κL & smaller gap;
Cs2AgBiCl6	2.75 (Ind.)	p-type	8.2×1019	180	0.95	0.29	0.48 (750 K)	Exceptional thermal durability;
Cs2AgSbBr6	1.64 (Ind.)	p-type	4.2×1019	230	2.05	0.16	1.08 (700 K)	Enhanced stereochemical activity
Cs2Ag(Bi0.75Sb0.25)Br6	1.85 (Ind.)	p-type	5.0×1019	225	1.98	0.13	1.15 (700 K)	Point-defect alloy scattering
Cs2NaBiI6	3.10 (Dir.)	n-type	6.0×1019	195	1.10	0.21	0.62 (650 K)	Lightweight monovalent site;
CsPbI3 (Pb Reference)	1.73 (Dir.)	p-type	3.0×1019	220	2.10	0.35	0.85 (600 K)	Conventional baseline; toxic lead content
Bi2Te3 (Commercial benchmark)	0.15 (Dir.)	p/n-type	3.0×1019	210	4.20	0.70	1.05 (350 K)	Industry standard for room temperature K.

CONCLUSION

Lead-free double perovskites (*A*2*MIMIIIX*6) represent a viable, environmentally compliant platform for solid-state waste heat recovery, resolving the critical toxicity and chemical instability limitations inherent to lead-based halide perovskites. Through an integrated analysis of electronic band structures, vibrational dynamics, and semiclassical carrier transport, this study demonstrates that ordered heterovalent rock-salt arrangements provide a natural decoupling of electronic and thermal pathways.

The prominent lattice anharmonicity, dense low-energy optical rattling modes of interstitial cations, and large atomic mass contrasts collectively suppress lattice thermal conductivities to glass-like regimes (κL<0.2 W m-1 K-1 at elevated temperatures), approaching theoretical minimum transport limits. Simultaneously, the inherent multi-valley band degeneracy near band extrema sustains high Seebeck coefficients ($|S| > 200\ \mu$V K -1) across degenerate carrier concentrations, yielding projected figures of merit (zT) exceeding unity in optimized systems such as p-type Cs2AgBiI6 and alloyed Cs2Ag(Bi1 -*x*Sb*x*)Br6.

Realizing the full potential of these materials in commercial thermoelectric generators demands targeted efforts to overcome fundamental drawbacks. Key research priorities include:

- Suppressing self-compensating native point defects to unlock stable degenerate doping (n>1019 cm -3)
- Designing compositional alloys to narrow fundamental indirect band gaps while minimizing halide phase segregation
- Mitigating high-temperature ionic drift and halogen sublimation via chemical encapsulation or grain-boundary passivation
- Developing mechanically resilient, chemically stable ohmic contacts capable of enduring sustained thermal gradients

  Addressing these transport and material-processing challenges will establish lead-free double perovskites as scalable, sustainable materials for intermediate-temperature solid-state heat-to-electricity conversion.

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