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First-principles investigations on the thermal transport and thermoelectric properties of anti-perovskite M_3OI and M_4OI_2 ($M = K, Rb$)

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The thermal transport and thermoelectric properties of anti-perovskite M_3OI and M_4I_2O ($M = K, Rb$) were investigated using first-principles calculations combined with solution of the Boltzmann transport equation. The two-phonon scattering channel was also considered. These structures formed M_6O octahedra, accompanied by a rattling motion of the O atoms. They exhibit ultra-low lattice thermal conductivity, ranging from 0.30 to 0.89 $W m^{-1} K^{-1}$ at room temperature. M_4I_2O demonstrates strong anisotropic thermal transport due to weaker bonding interactions along the zz direction, while M_3IO shows isotropic thermal conductivity. Specifically, Rb_4OI_2 has the lowest lattice thermal conductivity of 0.47 $W m^{-1} K^{-1}$ along the xx direction and 0.30 $W m^{-1} K^{-1}$ along the zz direction. Additionally, M_3IO possesses low lattice thermal conductivity of 0.52 $W m^{-1} K^{-1}$, attributed to the softening behavior of the TA branch at the M and R points. The electronic structure of M_3IO and M_4OI_2 reveals a multi-valley phenomenon in the valence band, resulting in a large Seebeck coefficient under p-type doping. Our results indicate maximum thermoelectric figure of merit (ZT) values of 1.91 for p-type Rb_3OI , and 1.41 for p-type Rb_4OI_2 along the zz direction at 900 K. Rb_3OI and Rb_4OI_2 were proposed as potential p-type thermoelectric materials.

KEYWORDS

first-principles, thermoelectric material, thermal transport, anti-perovskite, multi-valley phenomenon, ultra-low lattice thermal conductivity

1 Introduction

The energy shortage crisis is intensifying, making the search for sustainable and clean energy sources an urgent priority. Thermoelectric (TE) materials, which can convert thermal energy into electrical energy without generating additional pollution [1–3], show great promise in alleviating energy shortages and environmental pollution. Thermoelectric devices have the advantage of compact, lightweight, durable, and noiseless [4, 5]. The thermoelectric efficiency of materials is typically measured by the dimensionless figure of merit (ZT) [6]. High-performance thermoelectric materials must simultaneously exhibit a high thermoelectric power factor and low thermal conductivity [7]. However, the electronic conductivity and thermal conductivity are inherently coupled, which makes it challenging to achieve high electrical conductivity while maintaining a low electronic thermal conductivity. To overcome this challenge, researchers employ strategies such as introducing defects, alloys,

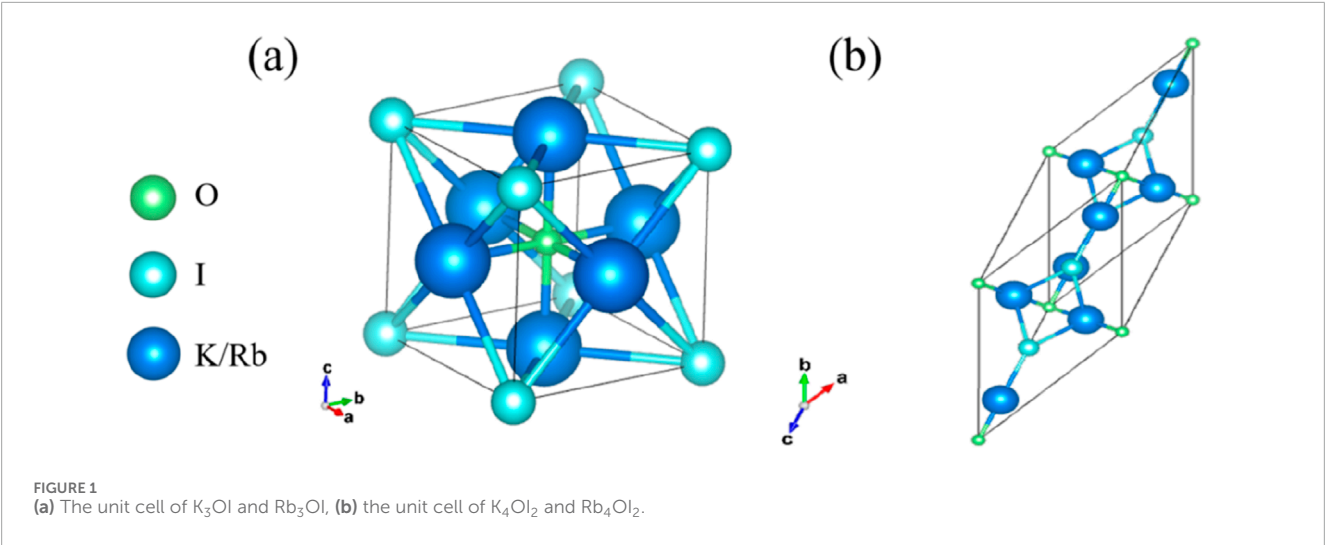


TABLE 1 Lattice constant (a), bond lengths, elastic constants (C), bulk modulus(B), Young's modulus(E), shear modulus(G), and Debye temperature(Θ) of the M_3OI and M_4OI_2 ($M = K, Rb$).

Structures	K_3OI	K_4OI_2	Rb_3OI	Rb_4OI_2
a(Å)	5.381	9.644	5.670	10.072
K_1/Rb_1-O (Å)	2.691	2.598	2.835	2.724
K_2/Rb_2-O (Å)	—	2.680	—	2.827
I-O (Å)	4.660	4.602	4.911	4.812
C11 (GPa)	42.152	35.934	35.913	30.348
C12 (GPa)	9.354	8.086	7.780	6.260
C44 (GPa)	12.236	6.520	9.552	5.077
C66 (GPa)	—	10.995	—	8.523
B (GPa)	20.287	17.509	17.158	14.729
E (GPa)	33.668	24.698	27.511	20.085
G (GPa)	33.668	9.763	11.158	7.891
Θ (K)	233.3	187.3	174.2	144.2

nanostructures, and suppressing the lattice thermal conductivity (κ_L) [8–14]. Therefore, searching low lattice thermal conductivity materials are important for improving the thermoelectric performance.

The perovskite structure has been classified as a “phonon glass, electron crystal” structure [15]. The octahedral framework vibrations and rattling behavior in anti-perovskite compounds induce strong anharmonic phonon scattering [16, 17], leading to intrinsically low lattice thermal conductivity. Some anti-perovskite derivatives, such as Rb_3AuO [18], Rb_3ITe [19], Ca_6NFSn_2 and Sr_6NFSn_2 [20] demonstrate exceptional thermoelectric

performance due to their ultra-low κ_L . For instance, the room temperature κ_L of Rb_3AuO is $0.73 \text{ W m}^{-1} \text{ K}^{-1}$, and the cubic phase of Rb_3ITe achieves an ultra-low κ_L of $0.16 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature. At 800 K, both materials attain $ZT > 3$, outperforming traditional inorganic thermoelectric materials such as Bi_2Te_3 [21], $SnSe$ [22], and lead chalcogenide compounds (with typical ZT values greater than 1) [23]. Moreover, Ca_6NFSn_2 and Sr_6NFSn_2 exhibit higher electrical conductivity than the halide perovskite $CsSnI_3$ [24]. When coupled with their low lattice thermal conductivity, the calculated ZT values achieve 1.9 and 2.3, respectively.

In this work, we employed first-principles calculations and the Boltzmann transport equation to study the thermal transport and thermoelectric properties of anti-perovskite M_3OI and M_4OI_2 ($M = K, Rb$). Due to their ultra-low lattice thermal conductivity, the dual-phonon channel model was discussed, which includes the contribution of diffuson-like phonon to the lattice thermal conductivity. The calculated κ_L values are about of $0.30\text{--}0.89 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature due to low phonon group velocity and short phonon lifetime. Furthermore, the multi-valley band structure increases the degeneracy of the energy bands, resulting in higher Seebeck coefficients (S) in p-type doping. The p-type anti-perovskite Rb_3OI achieves a maximum ZT of 1.91 at 900 K, demonstrating its potential for thermoelectric applications.

2 Computational methods

First-principles calculations were executed within the framework of the Vienna Ab Initio Simulation Package (VASP). It was performed using the Projector Augmented Wave (PAW) method, incorporating the Perdew–Burke–Ernzerhof (PBE) parametrization of the generalized gradient approximation (GGA) for the exchange correlation functional. The electronic properties were investigated based on the hybrid density functional theory (HSE06). The structures of the primitive cells were optimized until the atomic force converged to less than $10^{-4} \text{ eV/\AA}$. The energy cutoff and convergence criterion were set to 520 eV and 10^{-7} eV , respectively. A $9 \times 9 \times 9$ Γ -centered Monkhorst-Pack k-point mesh

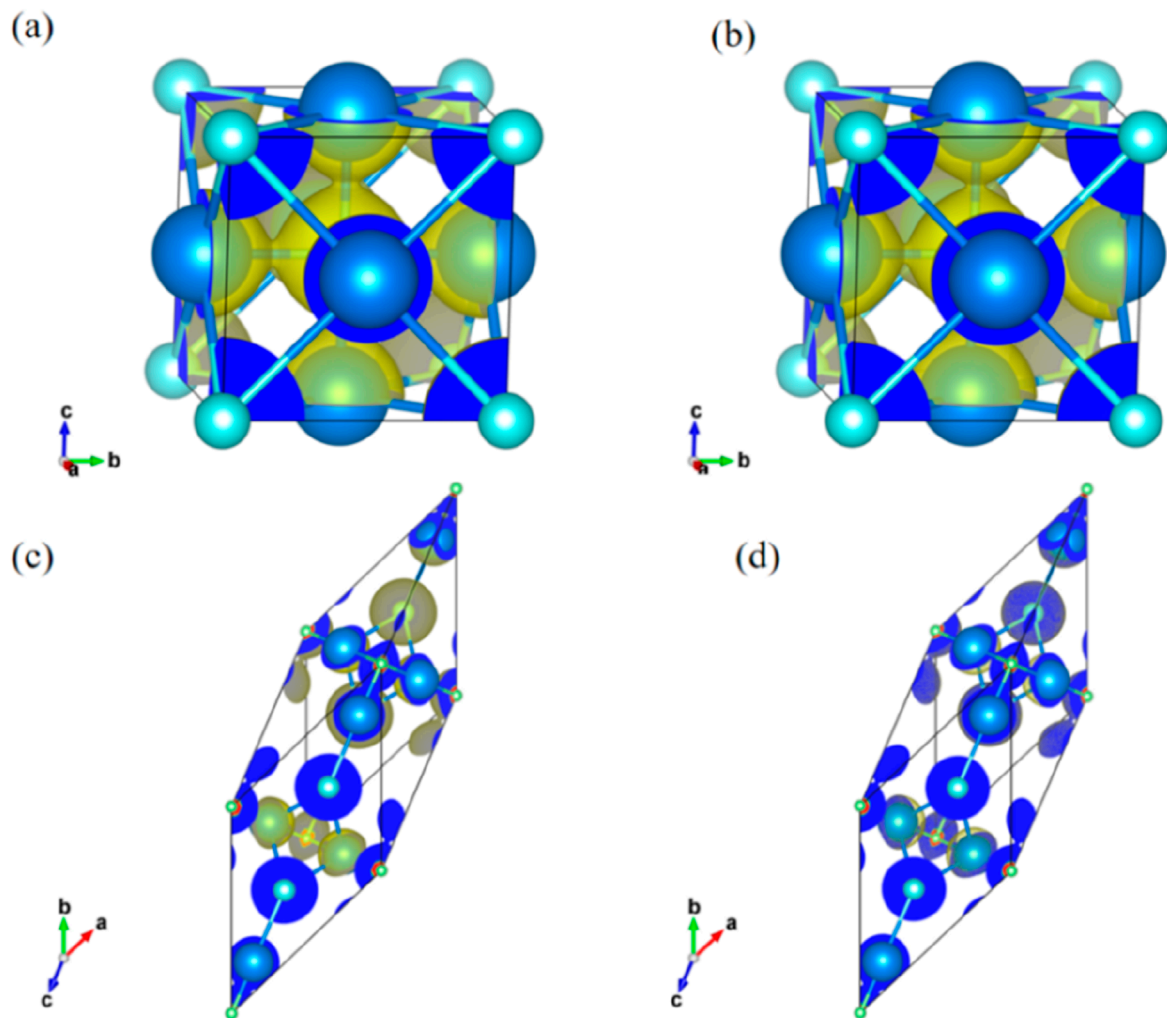


FIGURE 2
The charge density plot of (a) K_3OI , (b) Rb_3OI , (c) K_4OI_2 and (d) Rb_4OI_2 .

was employed to calculate the second- and third-order interatomic force constants (IFCs), which were subsequently utilized to study both harmonic and anharmonic phonon properties. Furthermore, the ShengBTE code was used to compute the lattice thermal conductivity of the materials *via* the phonon Boltzmann transport equation (BTE), as shown in the following Equation 1:

$$\kappa_t = \frac{1}{3} C_v v_g \lambda \quad (1)$$

where C_v is the specific heat, V_g is the group velocity, and λ is the mean free path. To ensure the convergence of the thermal conductivity calculations, a cutoff radius of 0.8 nm was implemented to limit the range of the third-order force constants. For the electrical transport properties, the *ab initio* scattering and transport (AMSET) software package was used to calculate carrier lifetimes, considering scattering processes due to acoustic deformation potential (ADP), ionized impurities (IMP), and polar-optical phonons (POP). The interpolation parameter 'interpolation_factor' is added to 110 to ensure the calculation accuracy and convergence. The final electron scattering time was derived using the following Equation 2, based on

Matthiessen's rule:

$$\frac{1}{\tau} = \frac{1}{\tau_{ADP}} + \frac{1}{\tau_{POP}} + \frac{1}{\tau_{IMP}} \quad (2)$$

3 Results and discussion

3.1 Structure and charge density

M_3OI ($M = K, Rb$) compounds exhibit simple anti-perovskite structures, following the general formula ABX_3 . As illustrated in Figure 1a, the crystal structures of K_3OI and Rb_3OI crystallize within the $Pm3m$ space group. In these structures, the alkali metals ($M = K, Rb$) occupy the X-sites within the unit cell, while the oxygen (O) ions occupy the B-sites. This arrangement results in M_6O octahedra formed by the oxygen anions and the alkali metal cations [25, 26]. The iodine (I) atoms are situated at the A-sites, which are located at the corners of the unit cell. Figure 1b depicts the crystal structure of anti-perovskite derivatives K_4OI_2

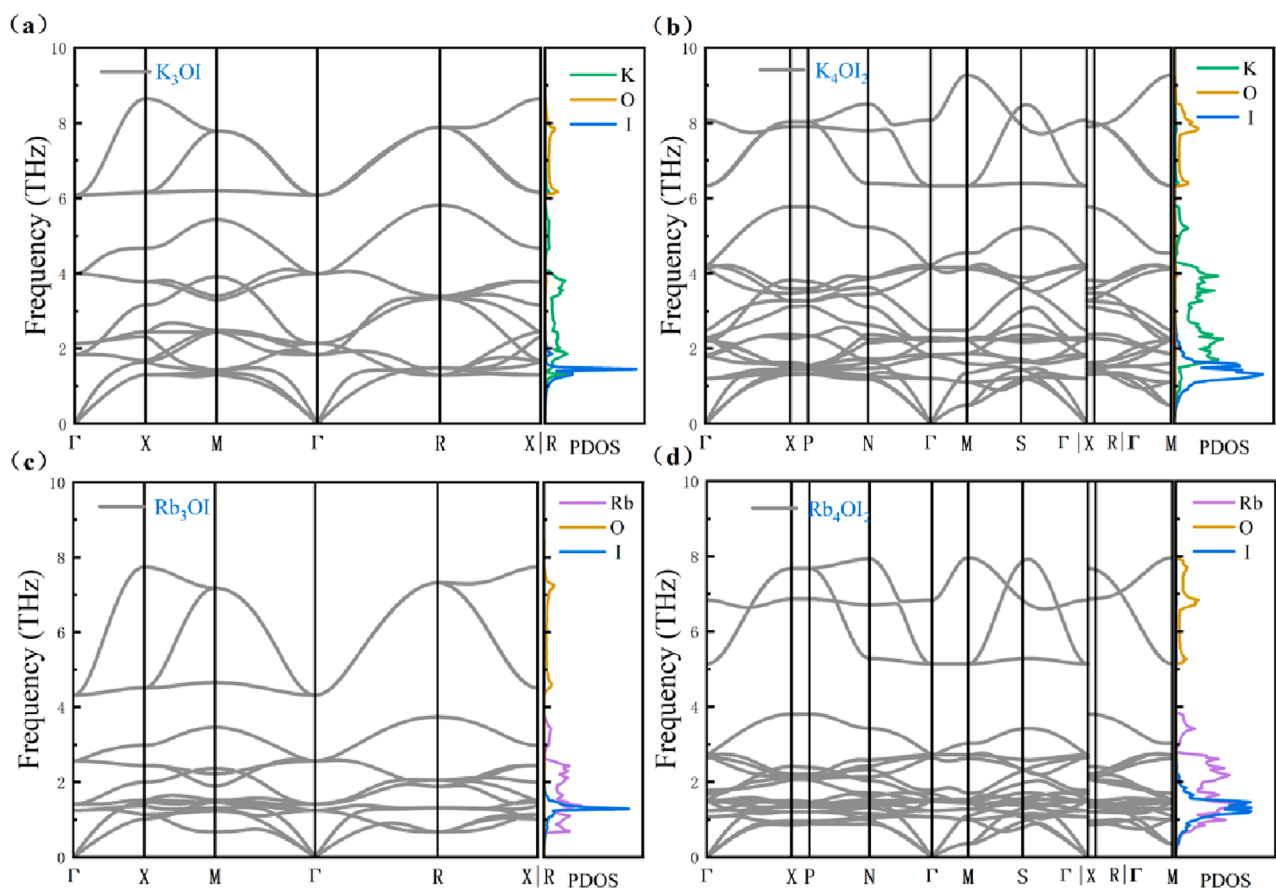


FIGURE 3
Phonon band and phonon density of states of (a) K_3OI , (b) K_4OI_2 , (c) Rb_3OI and (d) Rb_4OI_2 .

and Rb_4OI_2 , which bear resemblance to the $(La, Ba)CuO_4$ structure. These compounds belong to the tetragonal crystal system and crystallize in the space group $I4/mmm$. In this structure, two distinct alkali metal sites are presented, as noted in previous studies [27]. [Supplementary Figure S1](#) highlights the layered nature of this arrangement, where alternating M_3OI and MI layers are stacked along the z -axis(c), mirroring the structural arrangement seen in Na_4OI_2 [28].

The optimized lattice constants for these four structures are summarized in [Table 1](#). K_3OI has been successfully synthesized in experiments [29]. Additionally, [Table 1](#) provides bond lengths for each structure, along with key mechanical properties such as elastic constants, bulk modulus (B), Young's modulus (E), shear modulus (G), and the Debye temperature (Θ) [30]. The force constant for M_3OI ($M = K, Rb$) adheres to the mechanical stability criterion in [Equation 3](#), while M_4OI_2 ($M = K, Rb$) meets the mechanical stability criterion in [Equation 4](#). Therefore, all four structures are mechanically stable [31].

$$C_{11} - C_{12} > 0; C_{11} + 2C_{12} > 0; C_{44} > 0 \quad (3)$$

$$C_{11} > |C_{12}|; 2C_{13}^2 < C_{33}(C_{11} + C_{12}); C_{44} > 0; C_{66} > 0 \quad (4)$$

Debye temperature serves as an indicator of the bond strength of materials, with a positive correlation between these two parameters. Among the studied materials, K_3OI exhibits the highest Debye temperature of 233.3 K, followed by K_4OI_2 of 187.3 K and Rb_3OI of 174.2 K. The lowest Debye temperature of 144.2 K is observed in Rb_4OI_2 . This trend is consistent with the bond length of them. We find that all the Debye temperatures are significantly below the room temperature of 300 K, suggesting that the M_3OI and M_4OI_2 compounds exhibit pronounced anharmonic behavior.

The charge density in [Figure 2](#) shows a typical covalent bond charge distribution between the alkali metal M and the oxygen (O) element. Specifically, the strong covalent bond between the alkali metal M and O forms a stable M_6O octahedral framework structure. In contrast, the iodine (I) element exhibits a strong electronic localization phenomenon, with weaker bonding to other atoms. By comparing the charge densities in [Figures 2a,b](#) for K_3OI and Rb_3OI , and in [Figures 2c,d](#) for K_4OI_2 and Rb_4OI_2 , it can be observed that the $Rb-O$ bond is weaker than the $K-O$ bond, which is consistent with the results of bond length in [Table 1](#).

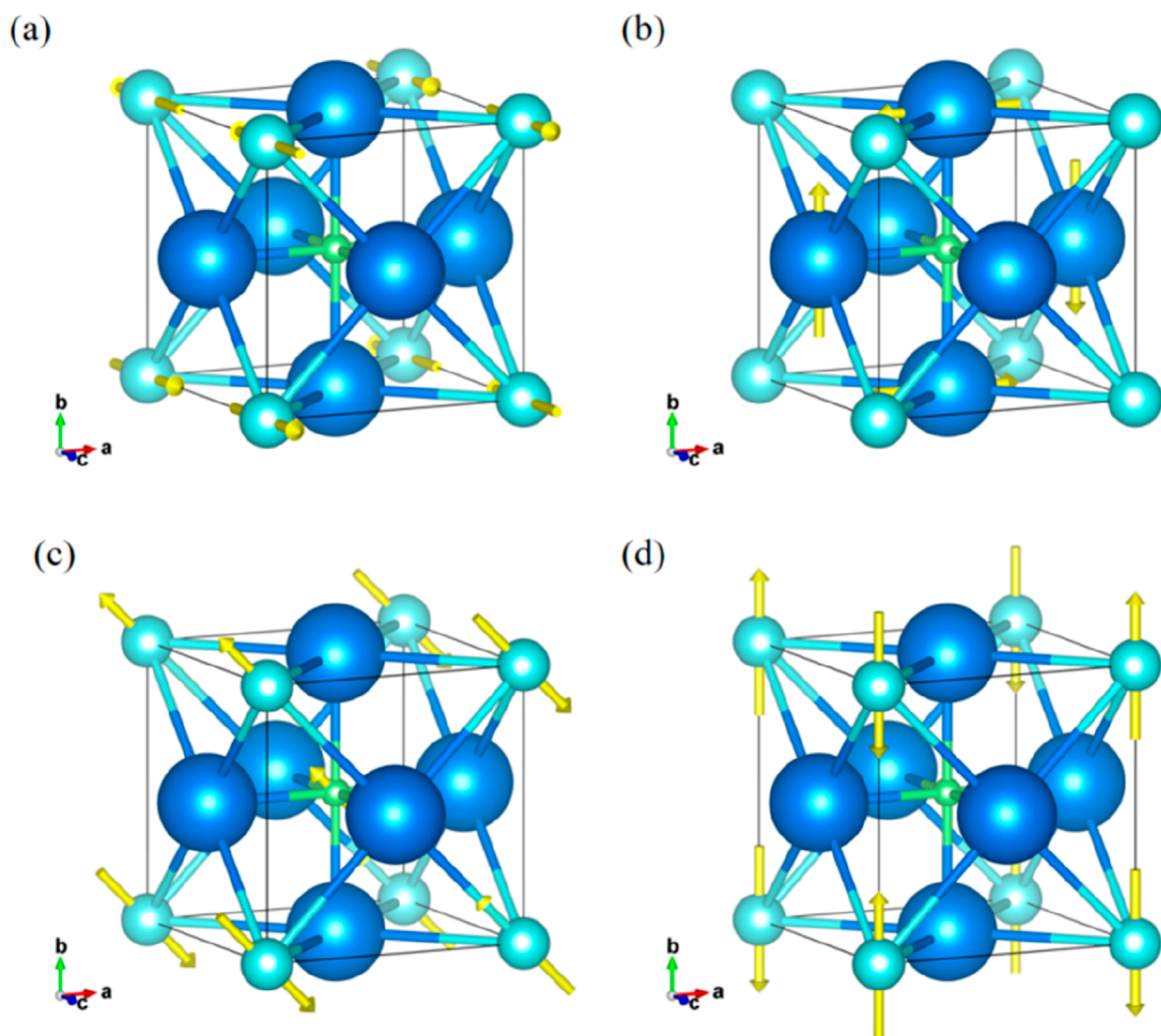


FIGURE 4
The vibrational modes of the Transverse Acoustic Branch (TA) at high-symmetry points M and R, and yellow arrows indicate the vibration directions, and their lengths represent the vibration amplitudes. **(a)** The vibrational mode of K_3OI at point M; **(b)** The vibrational mode of K_3OI at point R; **(c)** The vibrational mode of Rb_3OI at point M; **(d)** The vibrational mode of Rb_3OI at point R.

3.2 Thermal transport property

The phonon dispersion spectra show that K_3OI , K_4OI_2 , Rb_3OI , and Rb_4OI_2 exhibit no imaginary frequencies under the harmonic approximation in Figure 3, indicating that these materials are thermodynamically stable. The high-frequency optical branches are primarily contributed by the vibration modes of the oxygen (O) atoms, while the low-frequency optical and acoustic branches are dominated by the heavier iodine (I) and alkali metal (K, Rb) elements. The phonon dispersions for all four structures exhibit strong phonon-optical coupling within the low-frequency optical and acoustic branch regions, which is typically accompanied by peaks in the phonon density of states (PDOS). A comparison between Figures 3a,c reveals that the highest optical branch frequency for K_3OI is 9 THz, which is higher than the 8 THz for Rb_3OI . K_3OI exhibits stronger phonon dispersion, particularly in the acoustic branch, with the phonon group velocity for

K_3OI (0–1.44 THz) being significantly higher than for K_4OI_2 (0–1.19 THz). Similarly, Figures 3b,d show that the highest optical branch frequencies for K_4OI_2 and Rb_4OI_2 are 9 THz (K_4OI_2) and 8 THz (Rb_4OI_2), respectively, while the highest frequencies for the acoustic branches are 1.11 THz (K_4OI_2) and 1.00 THz (Rb_4OI_2). These materials have lower maximum acoustic branch frequencies compared to strong anharmonic materials such as Na_2TiSb [32] (~1.4 THz) and $SnSe$ [33] (~1.45 THz). Generally, when atoms of a similar structure are replaced with heavier elements, the phonon modes tend to shift to lower frequencies, which reduces the phonon group velocity and consequently suppresses the thermal conductivity. In the M_4OI_2 , the enhanced phonon-optical coupling relative to M_3OI provides more phonon scattering channels for the material. Notably, the phonon dispersion for Rb_3OI shows a pronounced softening of the TA branch at the M and R points, a phenomenon commonly observed in cubic perovskite structures. This ferroelectric-like vibration behavior is typically attributed to

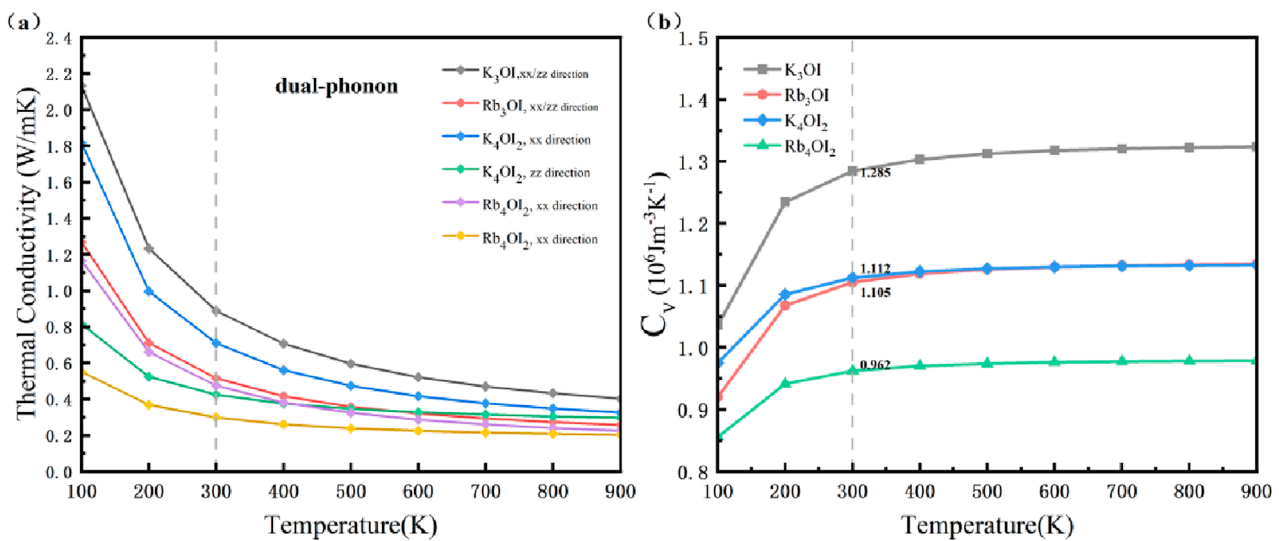


FIGURE 5
(a) The variation of lattice thermal conductivity (κ_L) with temperature after considering dual-phonon transport. (b) The variation of specific heat capacity (C_v) with temperature.

vibrations in the octahedral framework [34, 35]. Figure 4 illustrates the TA branch vibration modes at the high-symmetry M and R points for K_3OI and Rb_3OI . At the M point, the I atoms in K_3OI exhibit in-plane motion along the positive and negative z -axis (c) directions, while in Rb_3OI , the I atoms undergo in-plane motion within the xy (ab) plane with some rotational motion, and the O atoms exhibit a rattling behavior similar to that in octahedral structures. Figures 4b,d show that at the R point, the K atoms in K_3OI undergo opposing movements around the axis within the xy plane, leading to octahedral distortion, while in Rb_3OI , the I atoms exhibit in-plane motion along the positive and negative y -axis directions. In addition to the octahedral distortion [36], the rattling behavior within the octahedral cage is often considered a source of strong anharmonicity in anti-perovskite materials [37].

We employed the diffusion-like model of dual-phonon [38] with shengBTE to calculate the κ_L of these materials in the temperature range of 100–900 K, as shown in Figure 5a and Supplementary Figure S2. The lattice thermal conductivity decreases with increasing temperature. We find that Rb_4OI_2 along the zz (c) direction has the lowest thermal conductivity with and without considering the contribution of the diffuson-like phonon. At 300 K, when the two-phonon channel is neglected, it is $0.18 W m^{-1} K^{-1}$, lower than the $0.20 W m^{-1} K^{-1}$ reported for SnSe [22]. On the other hand, the K_3OI and Rb_3OI exhibit isotropic thermal conductivity while that for K_4OI_2 and Rb_4OI_2 show significant anisotropy. After considering the dual-phonon channel, the lattice thermal conductivity of K_3OI and Rb_3OI are $0.89 W m^{-1} K^{-1}$ and $0.52 W m^{-1} K^{-1}$, respectively. The lattice thermal conductivity of K_4OI_2 and Rb_4OI_2 is $0.71 W m^{-1} K^{-1}$ and $0.47 W m^{-1} K^{-1}$ along the xx direction, and $0.42 W m^{-1} K^{-1}$ and $0.30 W m^{-1} K^{-1}$ along the zz direction, respectively. At room temperature, the κ_L of these materials is comparable to the industry standard PbTe [39] and significantly lower than most oxide thermoelectric materials [40–43]. At

higher temperatures, κ_L remains below $1 W m^{-1} K^{-1}$, which is a characteristic feature of high-performance thermoelectric materials.

Heat capacity curve in Figure 5b shows that the specific heat capacity increases gradually with temperature in the range of 100–400 K. After 400 K, the heat capacities of the materials tend to converge. Over the entire temperature range, K_3OI and Rb_4OI_2 exhibit the highest and the lowest specific heat capacity, respectively. At 300 K, the specific heat capacities of K_4OI_2 and Rb_3OI are $1.112 \times 10^6 J m^{-3} K^{-1}$ and $1.105 \times 10^6 J m^{-3} K^{-1}$, respectively, while the heat capacity curves of the two materials nearly overlap beyond 400 K. Cumulative lattice thermal conductivity, as shown in Supplementary Figure S3, indicates that at 300 K, the lattice thermal conductivity is primarily contributed by phonon modes with an average free path (MFP) below 10 nm. ShengBTE results reveal that the high-frequency optical branches of these materials significantly contribute to the lattice thermal conductivity due to the strong phonon-optical coupling.

To further investigate the physical mechanisms for the thermal transport of these materials, Figure 6 plots the phonon relaxation time, phonon group velocity, scattering phase space, and Grüneisen parameter. As seen in Figure 6b, at 300 K, the phonon group velocity of K_3OI and K_4OI_2 along the xx direction is higher than that for Rb_3OI and Rb_4OI_2 in the acoustic branches and low-frequency optical branches (0–1.64 THz). In addition, the phonon group velocity of the M_3OI structure is higher than that of the M_4OI_2 . The difference in the phonon group velocities between K_3OI and R_3IO or K_4OI_2 , is mainly attributed to the increased effective atomic mass. This result aligns well with the phonon dispersion spectrum in Figure 3. The ultra-low lattice thermal conductivity of K_4OI_2 and Rb_4OI_2 in the zz direction, and their remarkable anisotropic structural properties, can be further explained by the softer bonds [44] and the lower phonon group velocity in the zz direction, as seen in Supplementary Figure S4.

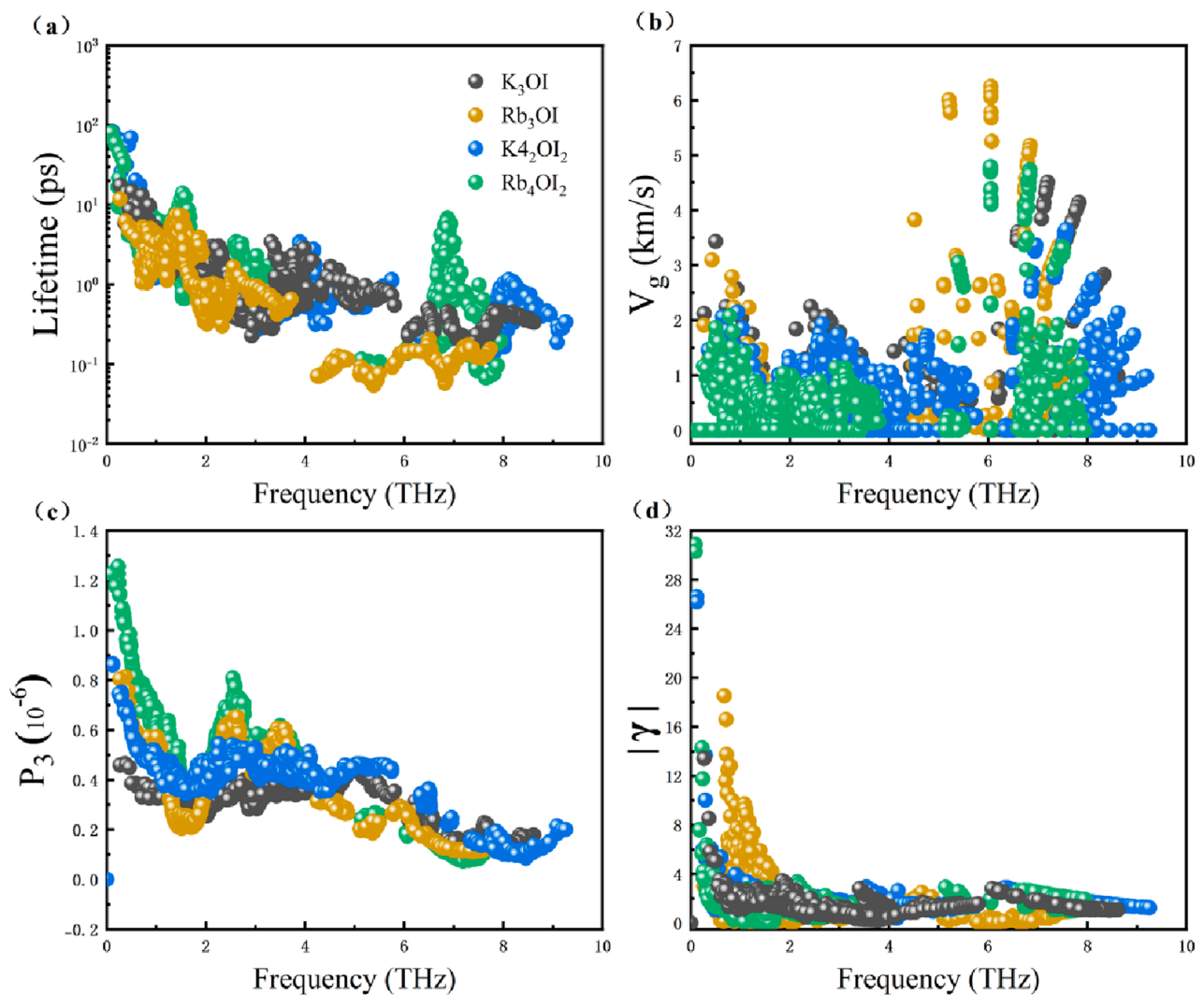


FIGURE 6

The variation curves of specific phonon thermal transport parameters with phonon frequency at 300 K. (a) Phonon relaxation time, (b) phonon group velocity in the xx direction, (c) P3 scattering phase space, (d) absolute value of the Grüneisen parameter.

Figure 6a presents the phonon relaxation times of these materials. Within the frequency range of the acoustic phonon, K_3OI (0–1.64 THz) and K_4OI_2 (0–1.42 THz) has overall higher phonon relaxation times compared to Rb_3OI (0–1.22 THz) and Rb_4OI_2 (0–1.11 THz), respectively. Moreover, the phonon relaxation times of K_4OI_2 and Rb_4OI_2 structures in the acoustic branch frequency range are larger than those of K_3OI and Rb_3OI structures. Next, we explored the P3 scattering phase space and Grüneisen parameter, as shown in Figures 6c,d. It indicates that K_3OI has the smallest scattering phase space, followed by K_4OI_2 , and Rb_4OI_2 exhibits the largest phase space in the low-frequency acoustic branch frequency range (0–1 THz). This phenomenon is attributed to the phonon dispersion becoming more confined in this frequency range (0–1 THz) as the average relative atomic mass increases, which makes it easier for phonon scattering to satisfy the energy conservation law. In the strong phonon-optical coupling frequency range, K_3OI exhibits smaller P3 compared to K_4OI_2 , and Rb_3OI is smaller than Rb_4OI_2 due to the increased number of low-frequency optical

branches, which strengthens the phonon-optical coupling and increases the scattering channels. Figure 6d displays the Grüneisen parameter at 300 K. The distribution is concentrated in the acoustic and low-frequency optical branch regions, with Rb_3OI showing a distinctly different parameter distribution. Its peak value occurs at ~1 THz, while the other three structures have their peaks near zero frequency. Rb_4OI_2 has a higher Grüneisen parameter than K_4OI_2 , and K_4OI_2 is higher than K_3OI . Although Rb_3OI has the lowest Grüneisen parameter in the acoustic branch (0–0.6 THz), its Grüneisen values in the 0.8–1.8 THz range are significantly largest, leading to the highest overall Grüneisen parameter and strongest phonon anharmonicity, and then the lowest phonon relaxation times. Additionally, the Grüneisen parameter distribution in Rb_3OI is influenced by the softening behavior of the transverse acoustic (TA) branch in the corresponding frequency range, which weakens the coupling with the low-frequency optical branch and leads to weaker phonon-optical coupling and a shift of the Grüneisen peak.

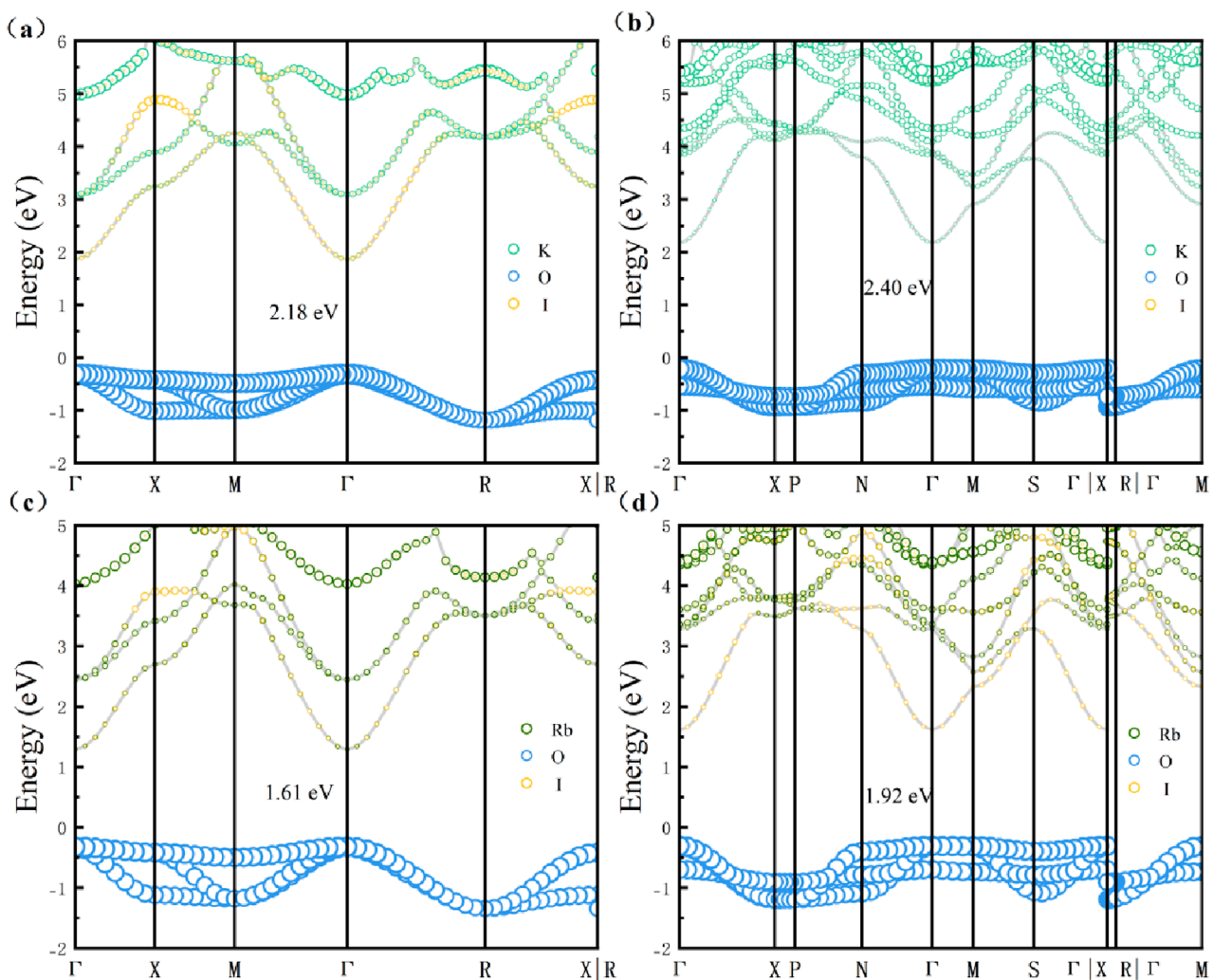


FIGURE 7
Projected electronic band diagram of (a) K_3OI , (b) K_4OI_2 , (c) Rb_3OI , (d) Rb_4OI_2 . The diameter of the circle is proportional to their orbital weight.

3.3 Electrical transport and thermoelectric properties

The electronic band structures were calculated using the hybrid functional HSE06. As shown in Figure 7. The electronic band gaps are 2.18 eV (K_3OI), 2.40 eV (K_4OI_2), 1.61 eV (Rb_3OI), and 1.92 eV (Rb_4OI_2), all of which are direct band gaps. The valence bands are primarily composed of the oxygen (O) orbitals, while the conduction bands are derived from the combined contributions of the alkali metals (K and Rb) and halogen (I) elements. The flat electronic band structure of the valence band indicates that it possesses a larger effective carrier mass, resulting in a lower carrier mobility. On the other hand, the significant band dispersion in the conduction band at the high-symmetry Γ point suggests that carriers near the conduction band exhibit a smaller effective mass and higher mobility. Notably, the valence band demonstrates a distinct multi-valley structure [45], which is often associated with high Seebeck coefficients of thermoelectrics [46].

The electronic transport properties of materials were studied using the AMSET software based on the electronic band structure. Figure 8 presents the computed electrical conductivity (σ), Seebeck coefficient (S), electronic thermal conductivity (κ_e), and power factor (PF) at different temperatures (300 K, 600 K, and 900 K). From Figures 8a,b, the electrical conductivity of n-type semiconductors is one order of magnitude higher than that of the corresponding p-type semiconductors. It is noteworthy that the electrical conductivity of the anisotropic material along the zz direction is the lowest, with a value ~ 1 S/m at a carrier concentration of 10^{19} cm^{-3} .

The Seebeck coefficient (S) of the p-type semiconductors is significantly higher than that of n-type ones, which can be attributed to the multi-valley phenomenon in the valence band of the electronic structure. For instance, at a carrier concentration of 10^{19} cm^{-3} , the Seebeck coefficient (S) of Rb_3OI ranges from 527 to 684 μVK^{-1} between 300 K and 900 K, which is higher than the 600 μVK^{-1} of Rb_3AuO [7]. And it is notably higher than the typical range

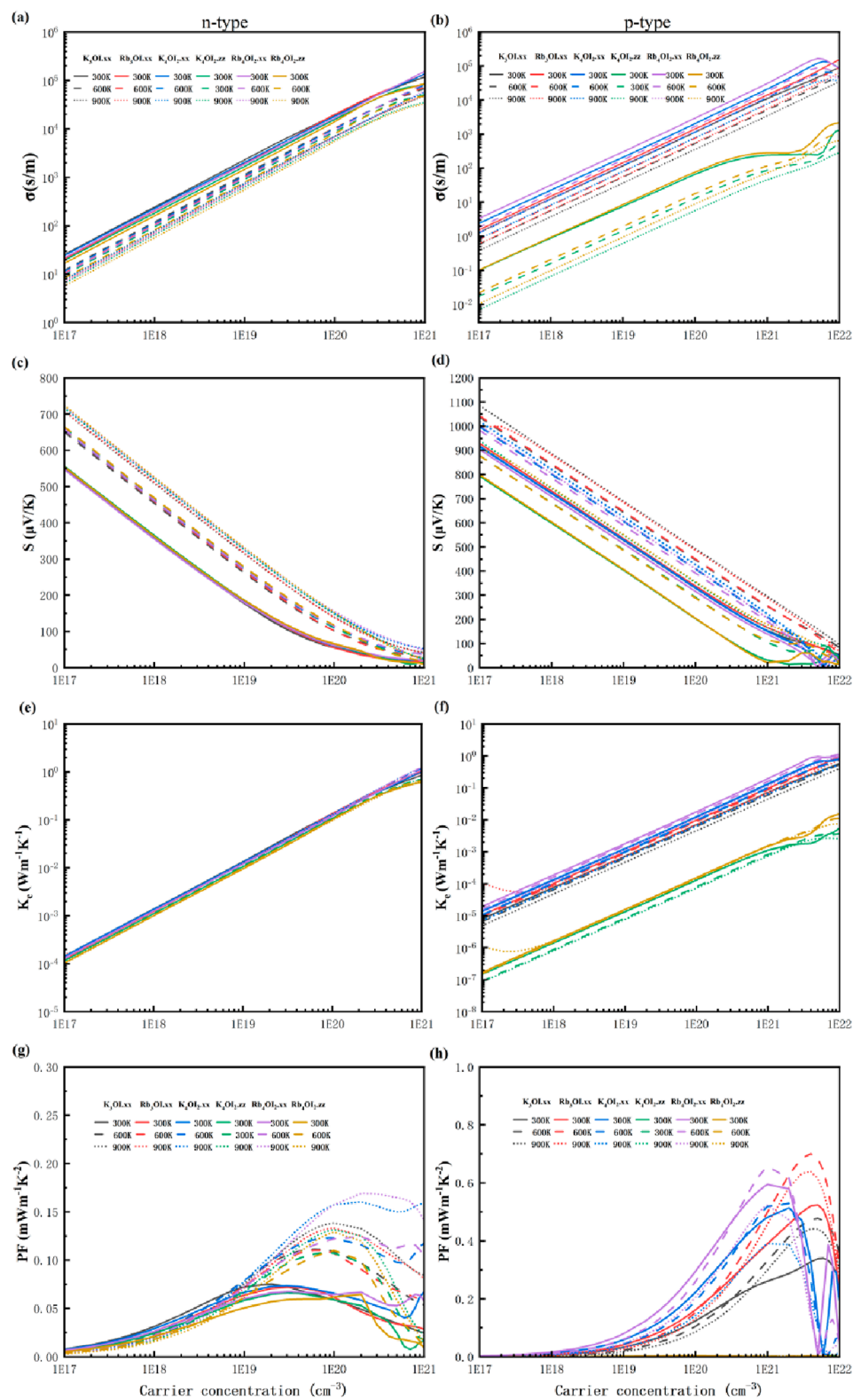


FIGURE 8

(a) The electronic conductivity (σ), (c) Seebeck coefficient (S), (e) electronic thermal conductivity (κ_e) and (g) power factor (PF) of n-type materials. (b) The electronic conductivity (σ), (d) Seebeck coefficient (S), (f) electronic thermal conductivity (κ_e) and (h) power factor (PF) of p-type materials.

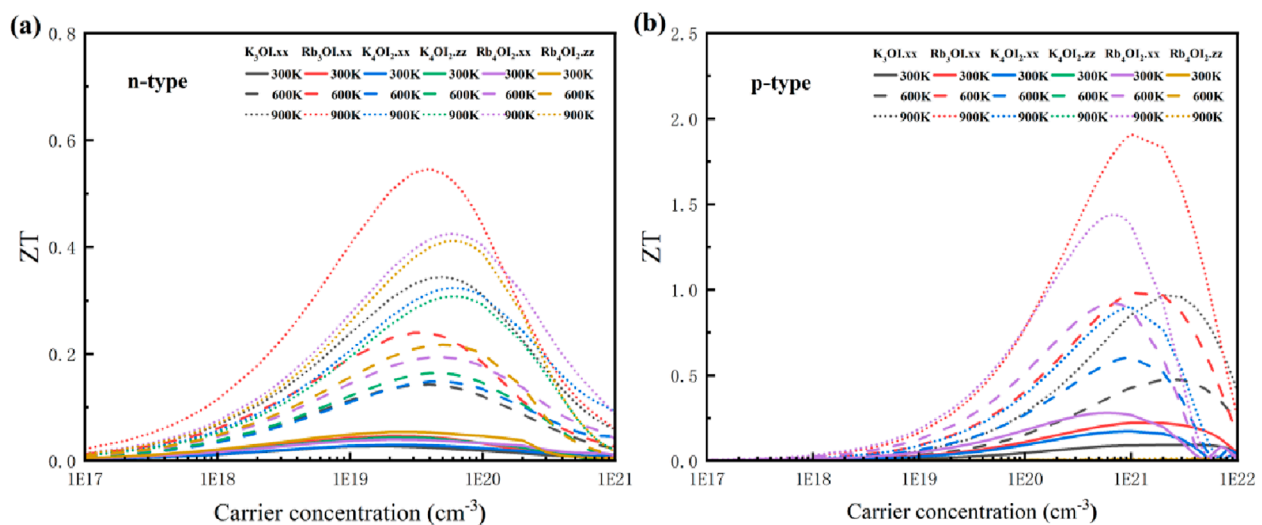


FIGURE 9
Thermoelectric figure of merit (ZT) of M_3OI and M_4OI_2 : (a) n-type, (b) p-type.

(200–300 $\mu V K^{-1}$) found in thermoelectric power materials [47]. Additionally, S decreases with increasing temperature as the carrier concentration decreases, which is consistent with the trend for the most semiconductor thermoelectric materials due to carrier excitation by heat.

According to the Wiedemann-Franz law, electrical conductivity is proportional to the electronic thermal conductivity. When doping concentration is low, the electronic thermal conductivity can be neglected. However, at higher doping concentrations, the electronic thermal conductivity becomes comparable to or even greater than the lattice thermal conductivity. The PF of the material is calculated based on the $S^2\sigma$ relationship. Due to the larger Seebeck coefficient (S) of the p-type semiconductors, the power factor of p-type materials is higher than that of n-type semiconductors, with the maximum value reaching $0.7 \text{ mW m}^{-1} \text{ K}^{-2}$ for Rb_3OI at 600 K, with a doping concentration of $4 \times 10^{21} \text{ cm}^{-3}$.

Subsequently, we computed the ZT values for these materials in Figure 9. At 900 K, Rb_3OI exhibits the highest ZT value of 1.91 for p-type doping at the carrier concentration of $1 \times 10^{21} \text{ cm}^{-3}$. The carrier scattering rate of R_3OI with a hole doping concentration of $1 \times 10^{21} \text{ cm}^{-3}$ were shown in Supplementary Figure S5. We found that the carrier scattering rate increased with the rise in temperature due to the thermal excitation of carriers and the scattering rate of carriers was mainly contributed by POP scattering.

Next, Rb_4OI_2 shows the maximum ZT value of 1.44 in the zz direction, with a p-type doping concentration of $7 \times 10^{20} \text{ cm}^{-3}$. In this system, the thermoelectric performance of the p-type semiconductor is superior to that of the n-type, which is attributed to the higher PF resulting from the larger Seebeck coefficient (S). Comparing with the ZT values of some inorganic halide perovskites of $CsPbI_3$ (0.45), $CsSnI_3$ (0.95), and $CsGeI_3$ (1.05) [48], Rb_3OI and Rb_4OI_2 have better thermoelectric performance. The results indicate that Rb_3OI and Rb_4OI_2 have promising potential for advanced thermoelectric device applications.

4 Conclusion

We investigated the thermal transport and thermoelectric properties of M_3IO and M_4I_2O ($M = K, Rb$). These structures formed M_6O octahedra and rattling behavior of the O atoms existed. The calculated Debye temperatures of these materials are obviously below the room temperature of 300 K. After considering the two-phonon channel, the lattice thermal conductivity ranges from 0.30 to $0.89 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature. Rb_4OI_2 has the lowest lattice thermal conductivity of $0.47 \text{ W m}^{-1} \text{ K}^{-1}$ and $0.30 \text{ W m}^{-1} \text{ K}^{-1}$ along the xx direction and the zz direction, respectively. Rb_3OI has the lattice thermal conductivity of $0.52 \text{ W m}^{-1} \text{ K}^{-1}$. M_3IO exhibits isotropic lattice thermal conductivity while that for M_4I_2O shows significant anisotropy. The phonon group velocity and specific heat capacity of the M_3OI structure are higher than that of the M_4OI_2 . However, M_3OI has lower phonon relaxation times due to the softening behavior of the TA branch at the M and R points. And then, their lattice thermal conductivity is comparable. Due to the multi-valley phenomenon in the valence band of the electronic structure, p-type M_3IO and M_4OI_2 have larger Seebeck coefficient (S). The calculated S of Rb_3OI ranges from 527 to $684 \mu V K^{-1}$ at a carrier concentration of 10^{19} cm^{-3} . We obtained the maximum ZT value of p-type Rb_3OI is 1.91 with the carrier concentration of $1 \times 10^{21} \text{ cm}^{-3}$ at 900 K, and that for p- Rb_4OI_2 is 1.41 in the zz direction at the doping concentration of $7 \times 10^{20} \text{ cm}^{-3}$. We propose that Rb_3OI and Rb_4OI_2 are promising candidates as p-type thermoelectric materials.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

HX: Visualization, Methodology, Writing – original draft, Formal Analysis, Conceptualization, Data curation, Software, Investigation. TH: Software, Writing – original draft, Investigation, Data curation. PZ: Writing – review and editing, Validation, Supervision. DL: Writing – review and editing, Funding acquisition, Formal Analysis, Validation, Supervision, Project administration.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fphy.2025.1619661/full#supplementary-material>

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