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High performance solid-state thermoelectric energy conversion via inorganic metal halide perovskites under tailored mechanical deformation

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Abstract Solid-state thermoelectric energy conversion devices attract broad research interests because of their great promises in waste heat recycling, space power generation, deep water power generation, and temperature control, but the search for essential thermoelectric materials with high performance still remains a great challenge. As an emerging low cost, solution-processed thermoelectric material, inorganic metal halide perovskites $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ under mechanical deformation is systematically investigated using the first-principle calculations and the Boltzmann transport theory. It is demonstrated that halogen mixing and mechanical deformation are efficient methods to tailor electronic structures and charge transport properties in $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ synergistically. Halogen mixing leads to band splitting and anisotropic charge transport due to symmetry-breaking-induced intrinsic strains. Such band splitting reconstructs the band edge and can decrease the charge carrier effective mass, leading to excellent charge transport properties. Mechanical deformation can further push the orbital energies apart from each other in a more controllable manner, surpassing the impact from intrinsic strains. Both anisotropic charge transport properties and ZT values are sensitive to the direction and magnitude of strain, showing a wide range of variation from 20% to 400% (with a ZT

value of up to 1.85) compared with unstrained cases. The power generation efficiency of the thermoelectric device can reach as high as approximately 12% using mixed halide perovskites under tailored mechanical deformation when the heat-source is at 500 K and the cold side is maintained at 300 K, surpassing the performance of many existing bulk thermoelectric materials.

Keywords inorganic metal halide perovskites, mechanical deformation, thermoelectrics, first-principle calculations, Boltzmann transport theory

1 Introduction

The development and progress of the modern society highly depend on the acquisition and efficient use of energy, especially when constrained by the current global energy crisis and environmental pollution problems [1–4]. According to recent studies, the global energy consumption of fossil fuels is growing rapidly, and 30%–60% of the energy consumed is wasted in the form of heat [5]. Therefore, recycling the waste heat and increasing the energy efficiency in industries and power plants are becoming more important. Thermoelectric generators have drawn attentions as they can directly convert heat into electricity based on the Seebeck effect [6–8], which is considered as a simple, effective, and environmentally friendly approach to harvest waste heat. Without moving parts, thermoelectric generators can also be greatly applied in space power generation, deep water power generation, and temperature control (see Figs. 1(a), 1(b)) due to their long-term stability and the noiseless feature [9–11]. The power generation conversion efficiency of thermoelectric generators is mainly dependent on the performance of thermoelectric materials (see Fig. 1(c)), where the figure of merit (ZT) can measure such thermoelectric performance and a higher ZT corresponds

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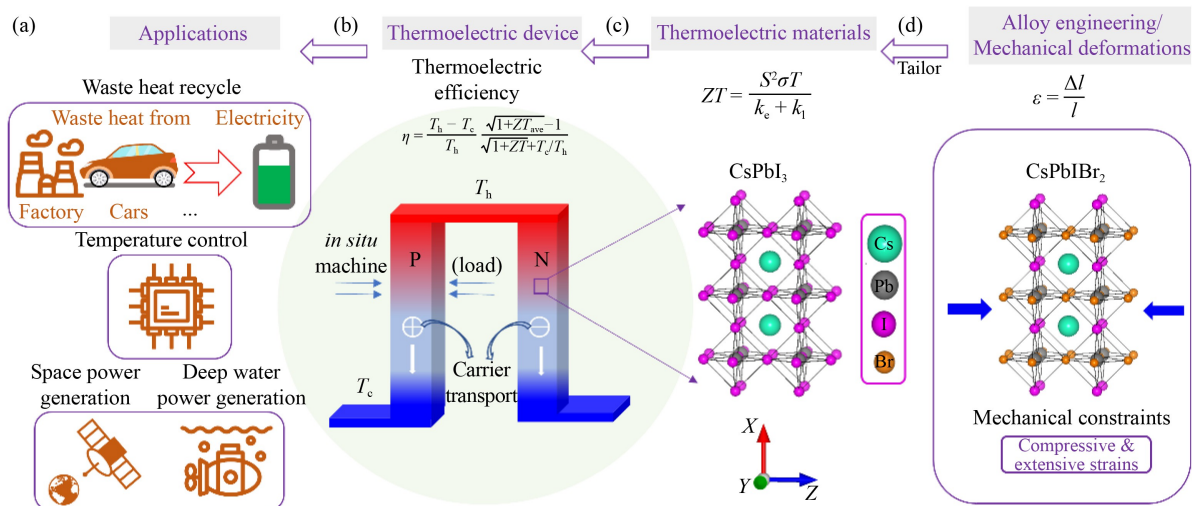


Fig. 1 Schematic diagram of perovskite-based thermoelectric materials, devices, and their potential applications.

(a) Potential thermoelectric applications; (b) thermoelectric device schematic diagram; (c) emerging halide perovskite CsPbI_3 as a potential N-type thermoelectric material; (d) representative polymorphic mixed halide perovskite at Br compositions $x = 4/6$ of $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$. (The mechanical deformation effect in combination with alloy engineering were used to tailor the transport properties, and the arrows denote the anisotropic strain directions. A complete set of polymorphic $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ structures is shown in Fig. S1.)

to a high energy conversion efficiency. ZT is defined as $ZT = S^2 \sigma T / (k_e + k_l)$, where S , σ , T , k_e and k_l are the Seebeck coefficient, electric conductivity, temperature, electronic and lattice thermal conductivity, respectively. The coupling of these parameters poses a great challenge to development of thermoelectric materials with a high performance.

Among the numerous thermoelectric materials, emerging metal halide perovskites and their derivatives have attracted much attention since they were first introduced into the thermoelectric field [12–14]. Eperon et al. [15] first demonstrated that cubic CsPbI_3 perovskite is very stable at low temperature for 200 days when stored in inert air. Kulbak et al. [16] found that devices fabricated with CsPbBr_3 are more stable than MAPbBr_3 -based ones. Wang et al. [17] discovered that compositional tuning of perovskites (such as the X-site halide substitution) can further improve their moisture stability. In addition, recent experimental studies have demonstrated the more improved material stability of all-inorganic mixed halide perovskites $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ than their pure counterparts [18]. Moreover, to suppress unwanted phase transition, stabilize the perovskite crystal structure, and tailor the thermoelectric performance, mechanical deformation treatment (see Fig. 1(d)) has been extensively utilized and investigated [19,20]. Li et al. [21] proposed that strain engineering strategy can effectively prevent the phase transition of CsPbI_3 based on DFT calculation results. Furthermore, Yalamdha et al. [22] found that CsSnX_3 ($X = \text{I}, \text{Br}, \text{Cl}$) displays a surprising band inversion behavior under pressures. Zitouni et al. [23] predicted the reduced band gaps in CsPbX_3 compounds under strains using first principles. Rahman and Giri [24] found that uniaxial tensile strain

leads to ultra-low thermal conductivities for hybrid organic-inorganic perovskites, indicating the potential of mechanical deformation engineering to tune the physical properties of perovskites. For other thermoelectric material systems, many research groups found that the thermoelectric properties can be highly enhanced via mechanical deformation using first-principles calculations in combination with the Boltzmann transport theory [25–28]. Moreover, *in situ* machines have been widely developed to apply compressive and extensive strains on the bulk materials in experiment [29,30], suggesting that it is urgent and necessary to understand the mechanical deformation effects. However, there are still several unresolved issues regarding mechanical deformation problems. Particularly, there are very few investigations and discussions on the effects of mechanical deformation and compositional tuning on the thermoelectric properties of inorganic metal halide perovskites.

Motivated by the little existing understanding of the effect of mechanical deformation, the authors of this paper investigated the transport properties of the mixed halide perovskites. Combining first-principles density functional theory (DFT) calculations and the Boltzmann transport theory, they explored the compressive and extensive strain effect on the anisotropic carrier (electron/hole) transport and thermoelectric properties of mixed halide perovskites $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$. The electronic band structures revealed that halogen mixing alone, even without mechanical deformation, would lead to orbital splitting at the band edge due to symmetry-breaking, leading to a remarkable thermoelectric ZT of up to approximately 1.7 at 300 K. Upon mechanical deformation (within $\pm 2\%$ strain, as considered here), the splitting of energy levels of the three-fold degenerated $6p_x$, $6p_y$, and $6p_z$ orbitals of

Pb at the conduction band minimum (CBM) were observed. The energy level of the corresponding splitting orbital would increase with an extensive strain or decrease with a compressive strain. Moreover, mechanical deformation induces a dramatic reconstruction of the CBM, changing the effective mass and the transport properties significantly. The Seebeck coefficient (S) tends to decrease upon splitting of the degenerated p-orbitals of Pb, while the electric conductivity (σ) along corresponding direction tends to increase if the orbital energy level decreases at lower carrier concentrations. Interestingly, mechanical deformation could reduce the optimal carrier concentration for achieving the maximum ZT at 300 K by more than 10 times, which would be beneficial to the doping process in real experimental design [31,32]. Anisotropic ZT values are very sensitive to the direction and magnitude of mechanical deformation, showing a wide-range variation of 20% to 400% (within $\pm 2\%$ strains, as considered herein, with a ZT value of up to 1.85) compared with the unstrained cases. This work highlights the fundamental mechanism and importance of mechanical deformation in the performance of metal halide perovskite devices.

2 Computational methods

The power generation efficiency of the thermoelectric device is mainly dependent on the performance of the thermoelectric materials of both N and P types as shown in Fig. 1. The power generation conversion efficiency of the thermoelectric device is expressed as $\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + ZT_{ave}}}{\sqrt{1 + ZT_{ave}} + T_c/T_h}$,

where T_h and T_c are the heat-source (hot-side) and heat-sink (cold-side) temperature of the device, and ZT_{ave} is the average ZT of the thermoelectric material, which can be tailored effectively via alloy engineering and mechanical deformation effect. In Ref. [33], it is demonstrated that the halide perovskite CsPbI₃ is a promising N-type thermoelectric material, and the Br atom substitutes the I halogen atom, forming the mixed halide perovskites alloy CsPb(I_{1-x}Br_x)₃, is promising to enhance the thermoelectric performance. First, the substitutions are from a starting pseudo-cubic supercell with $2 \times 1 \times 1$ expansion of the cubic unit cell of CsPbI₃, and it causes 21 symmetry-nonequivalent polymorphic structures. A complete set of the optimized CsPb(I_{1-x}Br_x)₃ structures are demonstrated in Fig. S1. Then, mechanical deformation was imposed to tailor the transport properties further. The mechanical deformation (external strain) ε_i was introduced by varying the length of each supercell along axis i with the other two axes remaining unstrained, while the nuclei and electrons are allowed to relax freely in order to minimize internal forces and energies. The external strains applied on the inorganic metal halide perovskites range from -2% to 2% with an interval of 0.5% .

For DFT calculations, the Perdew-Burke-Ernzerhof (PBE) [34] functional and the projector augmented-wave (PAW) [35] formalism were used to conduct the geometry optimization and electronic structure calculations using the VASP [36] package. A plane-wave energy cutoff of 500 eV was used, and a pseudo-cubic supercell based on the $2 \times 1 \times 1$ expansion of a cubic unit cell was treated with a Γ -centered $4 \times 8 \times 8$ k -point mesh. Using the quasi-Newton (variable metric) algorithm [37], the lattice volume, shape, and the atomic positions of each configuration were fully optimized to minimize atomic forces below 1.0 meV/Å. The energy convergence criterion is 10^{-5} eV for the self-consistent field iteration. A denser $6 \times 12 \times 12$ k -point mesh was used for electronic band structure calculation. The scissor-operator approach [38] was applied to correct the PBE band gaps to the experiment values of CsPbI₃ (1.6 eV) [39] and CsPbBr₃ (2.25 eV) [40], since the PBE functional is known to underestimate the band gaps.

The thermoelectric transport properties (including relaxation time-normalized electric conductivity σ/τ and the Seebeck coefficient S , as well as the resulting power factors $PF = S^2\sigma$) were calculated according to the Boltzmann transport theory using BoltzTraP [41] based on the relaxation time approximation. To estimate the carrier relaxation time τ , the deformation potential theory [42–46], the Fröhlich model [47], and the Brooks-Herring approach [48] were used to describe the scattering processes between charge carriers with longitudinal acoustic (LA) phonons, polar longitudinal optical (LO) phonons, and ionized impurities, respectively, and the details are presented in Electronic Supplementary Material. Note that τ was estimated using external strain-free CsPb(I_{1-x}Br_x)₃ structures as the reference in the deformation potential theory because only small strains (up to $\pm 2\%$) within the elastic deformation region of metal halide perovskites [49] were considered here. Since the above three relaxation time models do not involve mechanical deformation effect, the τ values predicted for unstrained CsPb(I_{1-x}Br_x)₃ were used here, whose details can be found in Ref. [33].

The Klemens phonon model [50,51] and the Wiedemann-Franz law [52] were used to calculate the lattice thermal conductivity and electronic thermal conductivity (based on the computed electric conductivity), respectively. The Klemens phonon model was used to describe variations in the lattice thermal conductivity due to halogen mixing, while the mechanical deformation effect on lattice thermal conductivity was not considered here. Generally, since the lattice thermal conductivity normally decreases with tensile strain for bulk semiconductors, it is expected that even higher ZT values can be achieved if the mechanical deformation effect is considered in phonon transport. Therefore, the underestimated (lower-limit) ZT values were reported only due to enhanced electronic transport properties under tensile strain

[53,54]. But it should also be noted that, for more special materials, such as two-dimensional materials, anomalous responses in thermal conductivity by tensile strains have been discovered [55–59]. For example, Hu et al. [56] found that the thermal conductivity of silicene first increases with extensive strain and then fluctuates at an elevated plateau. Tabarraei and Wang [59] also found that the thermal conductivity of boron nitride nanoribbons first increases and then decreases under stretching. Therefore, further investigations about the thermal conductivities under strain effect are expected.

3 Results and discussion

3.1 Electronic structures and mechanical properties under mechanical deformation

The electronic band structures of pure and mixed halide perovskites $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ (21 polymorphs) without mechanical deformation effect were studied first to understand the effect of halogen mixing. As exhibited in Fig. S2, the band gap tends to increase as the Br composition x increases, while the valence band maximum (VBM) and the CBM (band gap + VBM) decrease as x increases, consistent with previous computational studies [60,61]. As discussed in Ref. [33], for pure halide perovskites (CsPbI_3 , CsPbBr_3), the CBM is dominated by the three-fold degenerated $6p_x$, $6p_y$, and $6p_z$ orbitals of Pb (see Fig. S3(a)). However, in contrary to the degenerated CBM in the pure halide perovskites, the splitting of $6p_x$, $6p_y$, and $6p_z$ orbitals is observed in the CBM of mixed halide perovskites [33] (see Fig. S3(b)), indicating that the electronic structures and band gaps can be tailored by halogen mixing. Such orbital splitting is attributed to the intrinsic strains/stresses resulting from the different van der Waals (vdW) radii of the I and Br halogen ions [33]. However, since the intrinsic strains due to halogen mixing are inhomogeneous, there is no clear trend in the shifts of the $6p_x$, $6p_y$, and $6p_z$ orbitals of Pb upon halogen mixing. Therefore, the shifts in the band edge depend highly on the actual atomic arrangement of halogen atoms in each polymorph. Nevertheless, such orbital splitting is also traceable based on the detailed halogen arrangement in each polymorph. For the pseudo-cubic supercell considered here, the $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ polymorphs can be categorized into three groups based on different splitting characters of the Pb-6p orbitals without strains: (i) three-fold degenerated with energy levels of $6p_x$, $6p_y$, and $6p_z$ orbitals remain the same, (ii) energy level of only one orbital $6p_x/6p_y/6p_z$ shifts, while the other two almost remain the same as being two-fold degenerated, and (iii) all three orbitals split. In this paper, only one pure CsPbI_3 (three-fold degenerated) and one mixed CsPbIBr_2 (two-fold degenerated with maximum ZT value) perovskites were taken as examples to

investigate the mechanical deformation effects because of the space limitation and the similar varying tendency of the mechanical deformation effects on the transport properties for the other perovskites (see the ESM). The optimized structures of the pure (CsPbI_3) and the mixed (CsPbIBr_2) perovskites are shown in Figs. 1(c), 1(d) and the detailed lattice constants are listed in Table S1.

Interestingly, the band edge splitting is also observed when mechanical deformation is applied on even pure CsPbI_3 and CsPbBr_3 . Taking the electronic structures of CsPbI_3 for example (see Figs. 2(a)–2(e)), the $6p_x/6p_y/6p_z$ orbital of Pb shifts up (down) when the strain along the $X/Y/Z$ direction is negative (positive), showing a clear trend due to the controllable strain direction. To understand the origin of the trend above, the contour plots of the electron density projected onto the XY plane are displayed in Fig. 2(f) and the density of states (DOS) in Fig. S5. From the projected DOS, it can also be seen that the Pb- $6p_x$ orbital shifts up or down, attributing to the Rashba-type band splitting effect caused by electron polarization under mechanical deformation [62]. From the electron density, the overlap between Pb-s and I-p orbitals is more pronounced, caused by the applied negative (compressive) strain and the decreased interatomic distance. On the contrary, the electron density is more localized under positive (extensive) strain due to the increased interatomic distance and reduced interactions. Furthermore, the downward shift in the $6p_i$ orbital of Pb will reconstruct the CBM, leading to a dramatic change in the curvature of CBM along the corresponding direction i . For example, the CBM at the T -point of CsPbI_3 changes from the $6p_y$ and $6p_z$ orbitals to the $6p_x$ orbital under extensive strain along the X direction (see Fig. 2(c)), leading to the energy band bending (larger curvature) along the T - R (X) direction and a lower electron effective mass, while the band along the other two directions (T - Y and T - Z) remain almost unaffected compared with the unstrained case. The strain effect on CsPbBr_3 is not focused here due to the previously reported low ZT values of CsPbBr_3 compared with CsPbI_3 and mixed halide perovskites [33].

Mechanical deformation-induced band edge splitting is also observed in mixed halide perovskites, while it is entangled with the symmetry-breaking-induced band edge splitting due to halogen mixing (causing internal strains). For the mixed CsPbIBr_2 perovskite, there are two I atoms along X direction, while two Br atoms along Y and two Br atoms along Z directions, leading to a high intrinsic compressive strain along Y and Z directions. Therefore, for mixed halide CsPbIBr_2 perovskite, the CBM is dominated by the $6p_x$ orbital of Pb, while the other two-fold degenerated $6p_y$ and $6p_z$ orbital is on a higher energy level (Here, the band edge splitting in the unstrained mixed halide perovskites is depicted in Fig. S3(b) for reference and comparison.). Consequently,

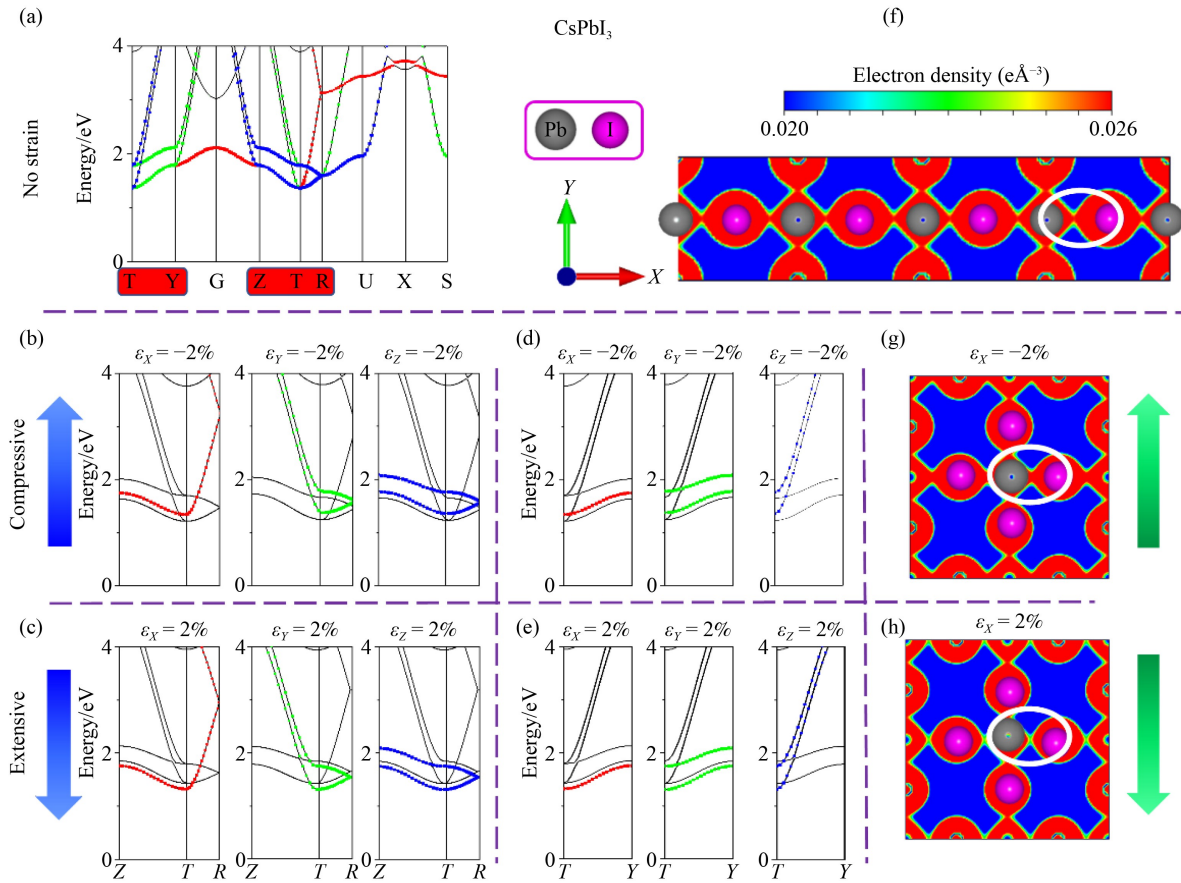


Fig. 2 Tailored electronic structures and electron densities of CsPbI₃ under mechanical deformations.

(a) Conduction band of CsPbI₃ without mechanical deformation; (b, c) electronic structures along *T-R* and *T-Z* directions under mechanical deformations; (d, e) electronic structures along the *T-Y* direction under compressive or extensive strains; (f-h) electron density projected onto the *XY* plane of CsPbI₃ under no, compressive, or extensive strains along *X* axis.

an extensive strain along *X* in the CsPbIBr₂ polymorph (Fig. 3(a)) will strengthen the splitting due to the downward shift of the 6p_x orbital. However, the extensive strains along *Y* or *Z* direction would make the original two-fold 6p_y and 6p_z orbitals become all three orbitals split. It is interesting to find that the mechanical deformation-induced band edge splitting in mixed halide perovskite can either reinforce or cancel out (weaken) the symmetry breaking-induced band edge splitting, depending on the direction, magnitude, and sign (compressive or extensive) of the strain. In addition, similar to the pure halide perovskites, a clear trend is found in mixed halide perovskites: extensive (compressive) strains along direction *i* will lead to downward (upward) shifts of the corresponding 6p_i-orbital of Pb. However, for the mixed halide perovskite CsPbIBr₂, the mechanical deformation along both *X*, *Y*, and *Z* directions would not dominate over the intrinsic strain, and the Pb-6p_x orbital maintains the CBM. For some other perovskites, however, the mechanical deformation effect would dominate over the intrinsic strain-induced band edge shifting (see Figs. S6–S8 and Supplementary Note) and the carrier effective

mass will suddenly change under strain if the mechanical deformation can overcome the symmetry-breaking effect to reconstruct the CBM, which depends on the actual atomic arrangement in each polymorph [33], and therefore, lead to a very clear trend in the resulting band edge shifting.

The Young's modulus, Shear modulus, Bulk modulus, and Poisson ratio of the two representative perovskites with and without mechanical deformation effect were then calculated, as it is essential to understand the mechanical properties for the device fabrications and engineering applications [63], especially the crack problems in thermoelectric device caused by the thermo-mechanical stresses. As is well known, the Young's modulus is used to determine the stiffness of the crystal, whereas Shear modulus, Bulk modulus, and Poisson ratio to deal with the material rigidity, plastic deformation, and ductile properties, respectively. Without mechanical deformation, as is shown in Fig. 4, the values of mechanical properties in the mixed halide perovskite CsPbIBr₂ are slightly higher than those of pure halide perovskite CsPbI₃, attributing to the higher strength of the

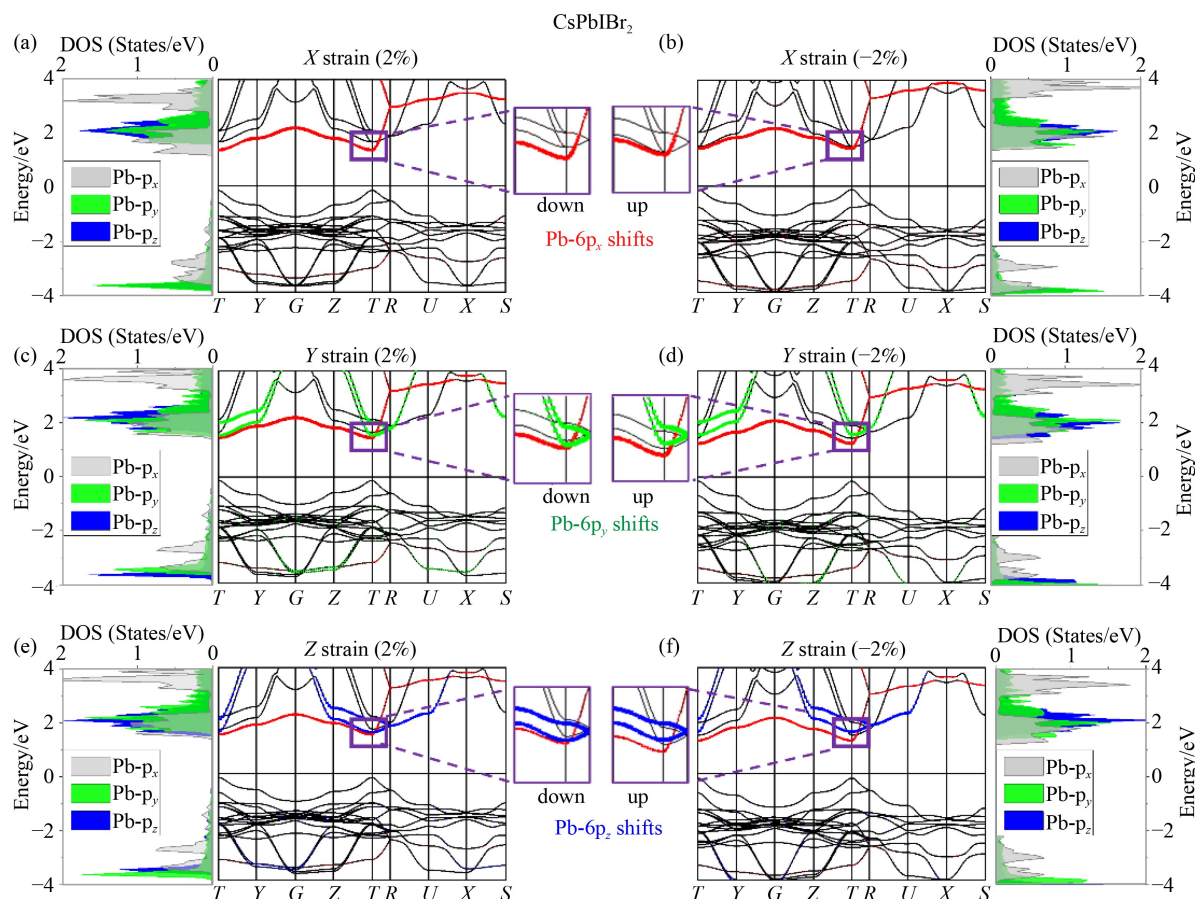


Fig. 3 Tailored electronic properties of CsPbIBr₂ under mechanical deformations.

(a, b) Electronic band structures and the projected Density of States (DOS) under extensive and compressive strains along X direction; (c, d) electronic band structures and the projected density of states (DOS) under extensive and compressive strains along Y direction; (e, f) electronic band structures and the projected DOS under extensive and compressive strains along Z direction. (The purple-framed figure is the enlarged electronic structures at CBM in order to see the orbital shifts more clearly, which shows a clear trend of the Pb-6p_{*i*} orbital shifts under mechanical deformation effect along i direction).

Pb-Br bond than that of the Pb-I bond. In addition, the different chemical bond type makes the mixed halide perovskite CsPbIBr₂ present anisotropic compared with the isotropic mechanical properties (along X , Y , and Z directions) of pure halide perovskite CsPbI₃. Furthermore, the mechanical deformation can also destroy the isotropic mechanical properties of the pure perovskite CsPbI₃ (see Fig. 4(b)) or aggravate/reduce the degree of the anisotropic properties of the mixed halide perovskite CsPbIBr₂ (see Fig. 4(d)), which can also be verified from the electron density (Fig. 2). Generally, the mechanical properties along the corresponding direction would increase (decrease) when the bond length decreases (increases) under negative (positive) strains, indicating that the mechanical properties can also be well tailored under mechanical deformation. The mechanical properties under mechanical deformation along other directions are shown in Figs. S9 to S10, and Table S2 summarizes detailed values of the mechanical properties.

3.2 Band edges, gaps, and carrier effective masses under mechanical deformation

The mechanical deformation-induced band edge splitting significantly modifies the band edges, band gaps, and carrier effective masses of both pure and mixed halide perovskites. Taking CsPbI₃ for example (Fig. 5), the mechanical deformation-induced variations in VBM and CBM do not depend on the direction of strain, showing an isotropic strain effect due to its high crystalline symmetry. The VBM of CsPbI₃ exhibits a linear correlation with strain along all three directions (Fig. 5(a)), attributing to the strain-proportional bonding/antibonding character of the Pb-6s and I-5p orbitals which are determined by the interatomic distance (see Fig. 2). However, the CBM and the band gap of CsPbI₃ (Figs. 5(a)–5(b)) exhibit a nonlinear trend with strain (showing a maximum at zero strain), attributing to the splitting of the degenerated Pb-6p orbitals. Specifically, as shown in Fig. 5(c), the energy levels of the Pb-6p_{*y*} and 6p_{*z*} orbitals

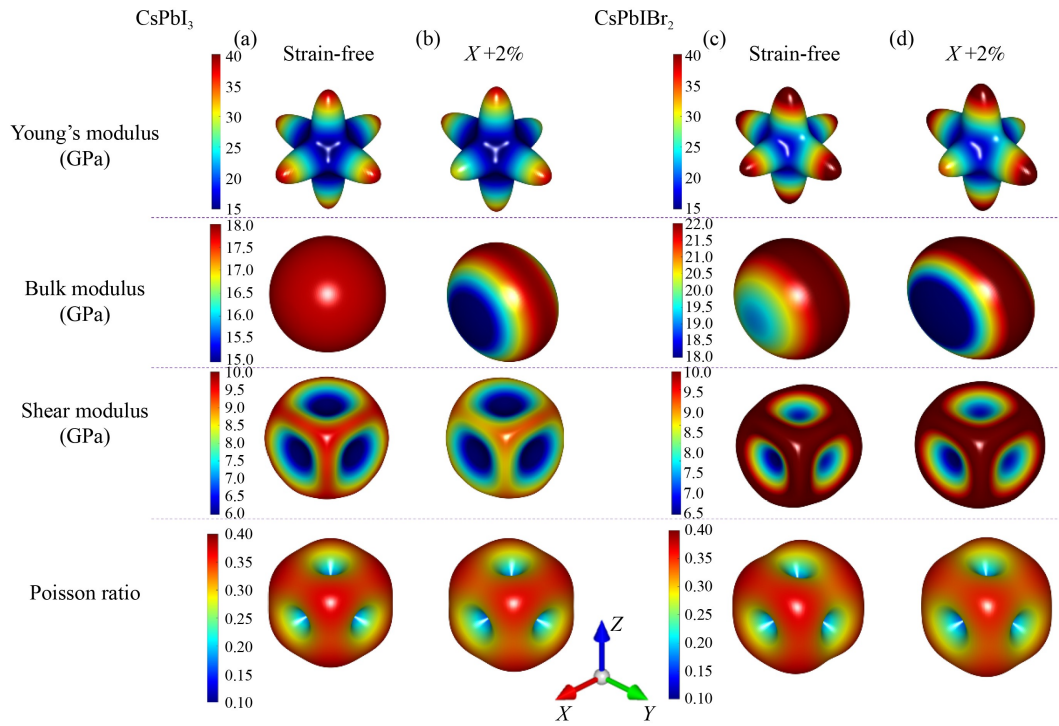


Fig. 4 Surface contours of the mechanical properties of CsPbI₃ and CsPbIBr₂.

(a, b) Mechanical properties of CsPbI₃ without and with +2% extensive strain along *X* direction illustrate in a 3D space; (c, d) mechanical properties of CsPbIBr₂ without and with +2% extensive strains along *X* direction illustrate in a 3D space.

remain two-fold degenerated with or without strain along the *X* direction, while they constitute the CBM under zero or compressive strains due to their positive linear correlation with strain. The energy of the split Pb-6p_x orbital crosses the energies of the Pb-6p_y and 6p_z orbitals at zero strain, and becomes the new CBM under extensive strain along *X* (the same trend is observed under the strain along *Y* or *Z* direction as shown in Fig. S11) due to its negative linearly correlation with strain. Such a crossover in the band edge orbital energies leads to different curvatures at the CBM as a function of strain (see Figs. 2(c)–2(d)), which exhibits a sudden decrease in the electron effective mass along the same direction of the extensive strain (see Fig. 5(d)). The effective mass computed from the band structure is expressed as $m^* = \hbar^2 / \frac{\partial^2 E}{\partial k^2}$, and therefore, the larger the curvature at the CBM, the smaller the effective mass value. Smaller electron effective masses lead to a higher electron mobility which is beneficial to the thermoelectric transport performance.

The same trend in band edge splitting and orbital energy shifting is observed in mixed halide perovskite CsPbIBr₂, as shown in Fig. 6, synergistically contributed by the symmetry-breaking and the mechanical deformation effects. It is noted that the mechanical deformation-induced variations in VBM do not depend on the direction of strain even in a highly anisotropic

structure (see Fig. 6(a)), attributing to the same strain effect (Fig. 2) involving the overlap between the Pb-6s and I-5p orbitals. On the other hand, the CBM and the resulting band gap present anisotropic properties, as a result of the combination of the band splitting caused by the mechanical deformation effect and the original splitting caused by halogen mixing for the Pb-6p orbitals (see Figs. 6(a)–6(b)). That is, the energy level of the Pb-6p_x orbital (CBM) would decrease under strain along *X* direction, while slightly increase along *Y* direction (see Figs. 6(c), 6(e)) (the same trend is observed under strain along *Z* direction as shown in Fig. S12). Furthermore, the electron effective masses of the representative mixed halide perovskite as a function of strain applied along different directions are shown in Figs. 6(d) and 6(f). Generally, the effective mass along the corresponding direction tends to slightly increase (decrease) with extensive (compressive) strain, while keeping steady along the other two directions for the mixed halide perovskite CsPbIBr₂ because there is no crossover of the orbitals (Pb-p_x maintain the CBM). However, the carrier effective mass will suddenly change under strain if the mechanical deformation effect can overcome the symmetry-breaking effect to reconstruct the CBM (see Fig. S8).

Structures with three-fold degenerated orbitals present the isotropic properties, and the two-fold degenerated orbital structures exhibit the same properties along the

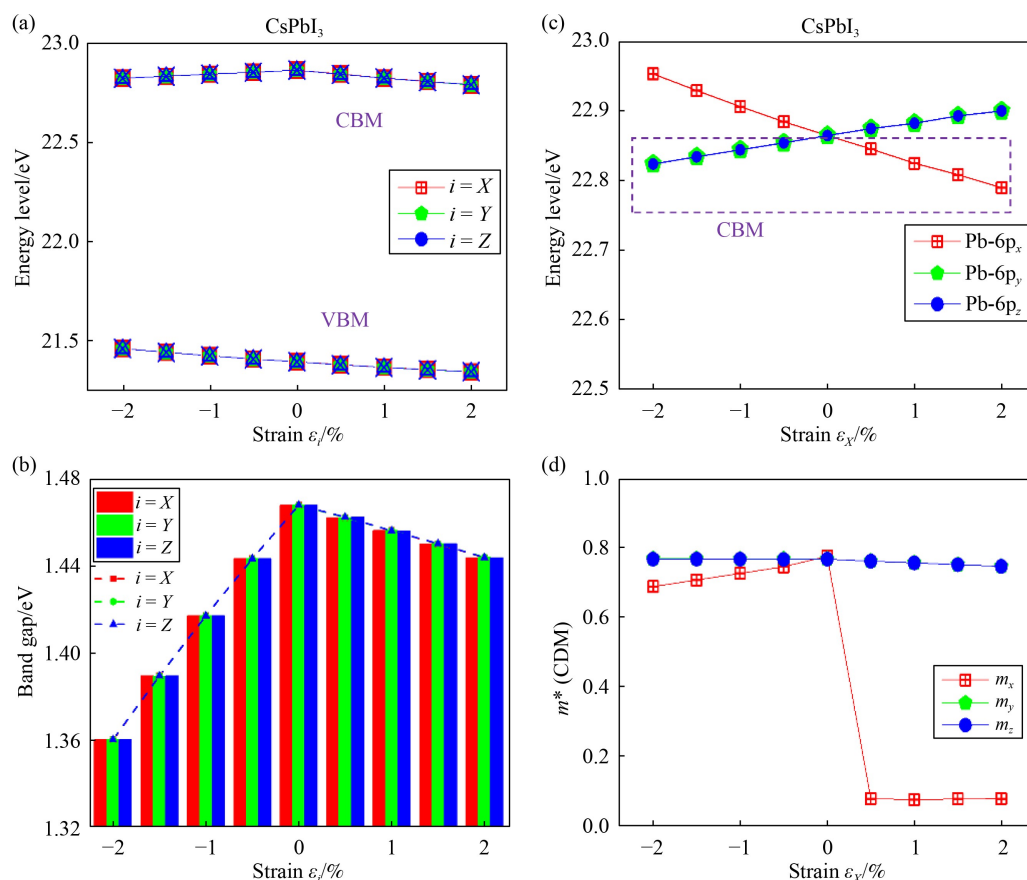


Fig. 5 Mechanical deformation-tunable band edges, band gaps, and carrier effective masses in CsPbI₃.

(a) CBM and VBM energy levels; (b) band gaps under strain along X, Y, and Z directions; (c, d) energy levels of 6p_x, 6p_y, and 6p_z orbitals of Pb and anisotropic electron effective masses m^* at CBM when strain applies along X direction.

corresponding two directions, while the properties of the structures with all orbitals split are mostly anisotropic. In addition, the band structures, band gaps, and even anisotropic transport properties (such as the effective mass) can be modulated by the splitting and shifts of the 6p_x, 6p_y, and 6p_z orbitals of Pb near the CBM. While this can be readily realized by intrinsic strains upon halogen mixing, mechanical deformation could enable controllable enhancement in transport properties along any direction needed. Therefore, to achieve the maximum transport properties, the magnitude, direction, and sign of the mechanical deformation should be analyzed concretely and applied according to specific polymorphs.

3.3 Thermoelectric transport properties under mechanical deformation

As the band structures, band gaps, and carrier effective masses are strain-tunable in mixed halide perovskites, it is expected that thermoelectric transport properties, including the Seebeck coefficient, electrical conductivity, power factor, and the resulting ZT values are controllable as well. In this paper, the mechanical deformation effect in n-doped (with electron as the charge carrier) mixed

halide perovskites at 300 K was mainly focused on because band splitting occurs at the CBM and higher ZT values were predicted in n-doped CsPb(I_{1-x}Br_x)₃ in Ref. [33]. It is expected that a similar temperature dependence would hold in thermoelectric transport properties of n-doped CsPb(I_{1-x}Br_x)₃ under mechanical deformation. Herein, “I-J” was used to denote the strain direction I and the resulting thermoelectric transport properties along dimension J. For the pure halide perovskite CsPbI₃ (three-degenerated Pb-6p orbital), the change in transport properties along a direction when a strain is applied along that same direction shares the same trend (i.e., X-X, Y-Y, and Z-Z cases are the same). This also applies to the orthogonal I-J cases, i.e., the change in transport properties for the X-Y (X-Z) case is similar to those for the Y-X (Y-Z) and Z-X (Z-Y) cases. Therefore, for the pure halide perovskite CsPbI₃, the mechanical deformation effect is shown only along one direction and it is presumed that the other two are similar.

For the CsPbI₃ perovskite with three-fold degenerated Pb-6p orbitals, the magnitude of the Seebeck coefficient S decreases as the magnitude of the strain increases along X because of the decreased level of degeneracy from three-fold to two-fold at 300 K (see Figs. 7(a)–7(c)). The

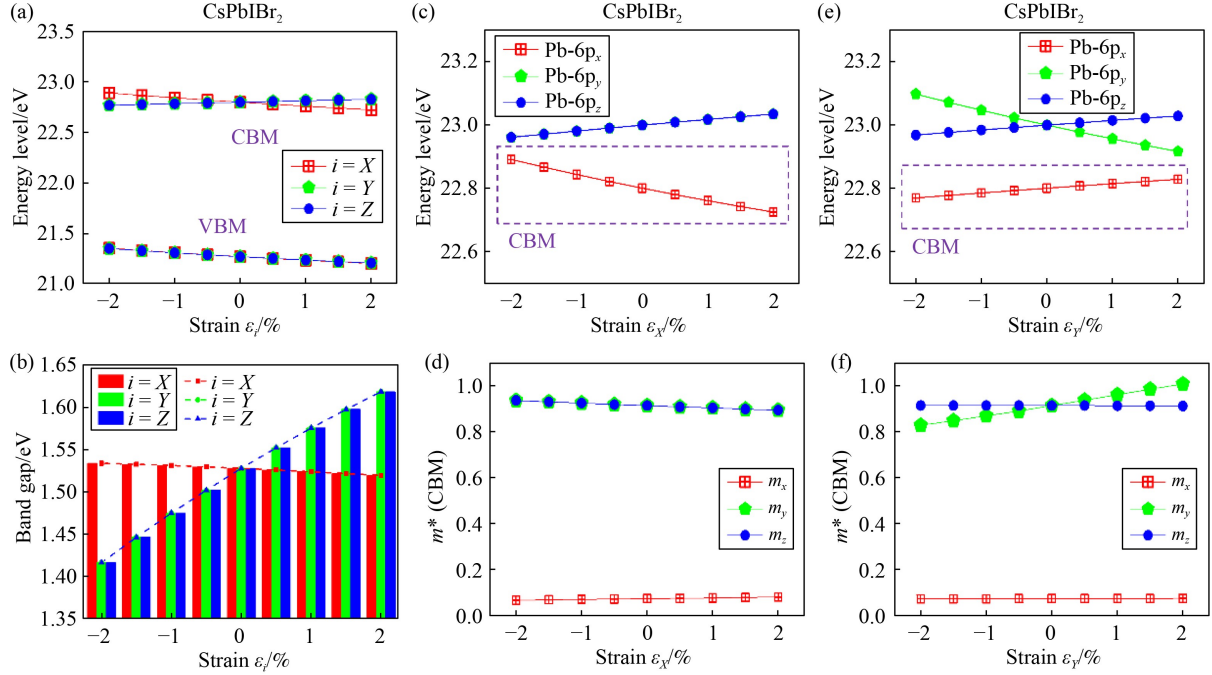


Fig. 6 Mechanical deformation-tunable band edges, band gaps, and carrier effective masses in CsPbIBr₂.

(a) CBM and VBM energy levels; (b) band gaps under strains along X , Y , and Z directions; (c–f) energy levels of $6p_x$, $6p_y$, and $6p_z$ orbitals of Pb and anisotropic electron effective masses m^* at CBM when strain applies along (c, d) X direction, and (e, f) Y direction.

Seebeck coefficient along X - X decreases more than those along X - Y and X - Z . A very different trend is observed in the electric conductivity σ , in which σ along X - X (X - Y and X - Z) increases (decreases significantly) when enlarging the strain at lower carrier concentrations, while that along X - X (X - Y and X - Z) decreases (increases slightly) gradually when enlarging the compressive strain (see Figs. 7(d)–7(f)), attributing to the combination of the carrier relaxation time-normalized electric conductivity σ/τ and the estimated carrier relaxation time τ (see Fig. S13). The carrier relaxation time-normalized electric conductivity σ/τ along X - X (X - Y and X - Z) increases (decreases significantly) when enlarging the extensive strain, while that along X - X (X - Y and X - Z) decreases (increases slightly) gradually when enlarging the compressive strain. The relaxation time remains stable as the strain varies, while it changes sharply when the effective mass changes dramatically (see Fig. S13(d)), which can be attributed to the fact that the polar optical relaxation time is dominant at a lower concentration, and the relaxation time would therefore increase sharply due to the small effective mass (almost massless) as the mechanical deformation applies.

The decrease in S and increase in σ along X - X with mechanical deformation reduce the optimal carrier concentration n_e for achieving the maximum ZT value significantly, by one order of magnitude from 10^{19} to 10^{18} cm⁻³ (see Fig. 7(g)). This is beneficial to meet the longstanding challenge in doping halide perovskites at high carrier concentrations in experiment due to their

self-compensating nature [31,32], although the maximum ZT values along X - X are only slightly enhanced from 0.5 without strain to 0.55 at an extensive strain of 2%. But it should also be noted that, even though the optimal carrier concentration decreases significantly, it poses a challenge to heavily dope perovskites in existing experiments. Therefore, further investigations on the impact from defects and heterovalent doping methods are expected. Interestingly, Kang and Wang [64] proposed that, for CsPbBr₃, most of the intrinsic defects induce shallow transition levels and small formation energies, which may lead to a high carrier concentration. Recently, Zhang et al. [65] have proposed that the deep defect level engineering concept is a strategy to optimize the carrier concentration. Ren et al. [66] also proposed that by introducing an intermediate-level impurity, the carrier concentration can be tailored and optimized simultaneously over a wide temperature range.

On the other hand, the maximum ZT values along X - Y and X - Z decrease quite a lot under extensive strains because of the slightly decreased Seebeck coefficient and significantly reduced electric conductivity, while the ZT values are only slightly enhanced under compressive strains (Figs. 7(h), 7(i)).

For the mixed halide perovskite of CsPbIBr₂, with only one Pb- $6p_x$ orbital shifts while the other two remain at the same energy level without mechanical deformation, such that transport properties along Y and Z directions are similar. Since the mechanical deformation-induced variations in S and σ follow the same trend mentioned

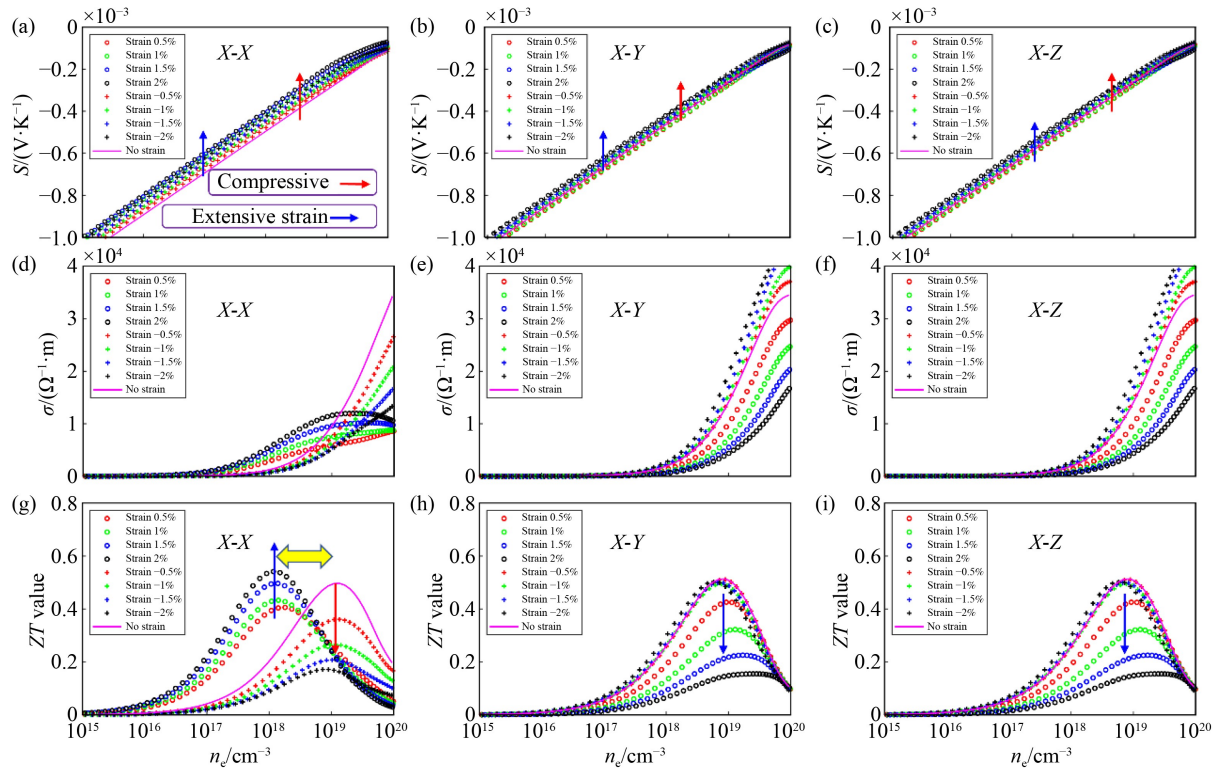


Fig. 7 Transport properties of CsPbI₃ at 300 K under mechanical deformations.

(a–c) Anisotropic Seebeck coefficient S ; (d–f) anisotropic electric conductivity σ ; (g–i) anisotropic ZT values of CsPbI₃ as a function of the carrier concentration n_e , when a strain is applied along the X dimension at 300 K. (The anisotropic properties along X , Y , and Z are labeled by X - X , X - Y , and X - Z , where the first X denotes the strain direction and the second symbol denotes the carrier transport direction).

above (resulting from orbital shifts), the computed anisotropic ZT values are only shown as a function of carrier concentration n_e when strains are applied along different directions (The detailed transport properties are shown in Figs. S14–S17). As shown in Figs. 8 and S17, the varies in transport properties and the resulting ZT values for the Y - Y (Y - Z , X - Y) case are similar to those for the Z - Z (Z - Y , X - Z) cases because of the two-fold degenerated Pb-6p_y and 6p_z orbitals. Then, as discussed above, extensive strains shifting down the 6p_y and 6p_z orbital or compressive strains shifting up the 6p_x orbital would weaken the symmetry-breaking effect, however, the mechanical deformation effect is not strong enough to cancel out the symmetry-breaking effect completely. Therefore, the ZT values and the optimized carrier concentration to achieve the maximum ZT values exhibit little deformation effect, regardless of the strain direction, because of the steady effective mass and the maintained CBM (Pb-6p_x orbital). On the contrary, the sharply change of the optimal carrier concentration and the transport properties will be exhibited when the mechanical deformation covers the intrinsic strain effect (see Figs. S18–S20). Finally, the maximum ZT value can be achieved from about 1.7 (no strain) to 1.85 (under extensive strain along X or compressive strain along Y and Z directions) along X direction.

The thermoelectric transport properties and ZT values are mechanical deformation-tunable in inorganic metal halide perovskites, either by mechanical deformation or intrinsic strains caused by halogen mixing. These two factors can be combined synergistically to achieve remarkable ZT values in CsPb(I_{1-x}Br_x)₃. For pure CsPbI₃ perovskite with three-fold degenerated Pb-6p orbitals, the maximum ZT values can be enhanced from about 0.5 without strain to 0.55 with a strain of $\pm 2\%$ (e.g., X - X , Y - Y and Z - Z). For mixed halide CsPbIBr₂ perovskite with two-fold degenerated Pb-6p orbitals, the maximum ZT values can be enhanced from 1.7 without strain to 1.85 with a strain of $\pm 2\%$ (e.g., X - X and Y - X / Z - X). Such high ZT values (1.85 at 300 K) is even higher than the best commercialized and most reported Bi₂Te₃ based materials at room temperature, where the highest reports are the Fe-doped Bi_{0.4}Sb_{1.6}Te₃ (experimental $ZT = \sim 1.4$) [67], and Bi_{0.5}Sb_{1.5}Te₃ (experimental $ZT = 1.72$) [68]. For metal halide perovskites, the majority of the experimental reports on ZT values are Sn-based [14]. In contrast, the reported ZT values are still low (below 0.2) for metal halide perovskites, and the highest reported ZT value is 0.19 for (F4-TCNQ)-doped FASnI₃ [69]. Therefore, more investigations and effects are urgently needed to experimentally verify the appealing theoretical reports [14]. Finally, the power generation efficiency of the

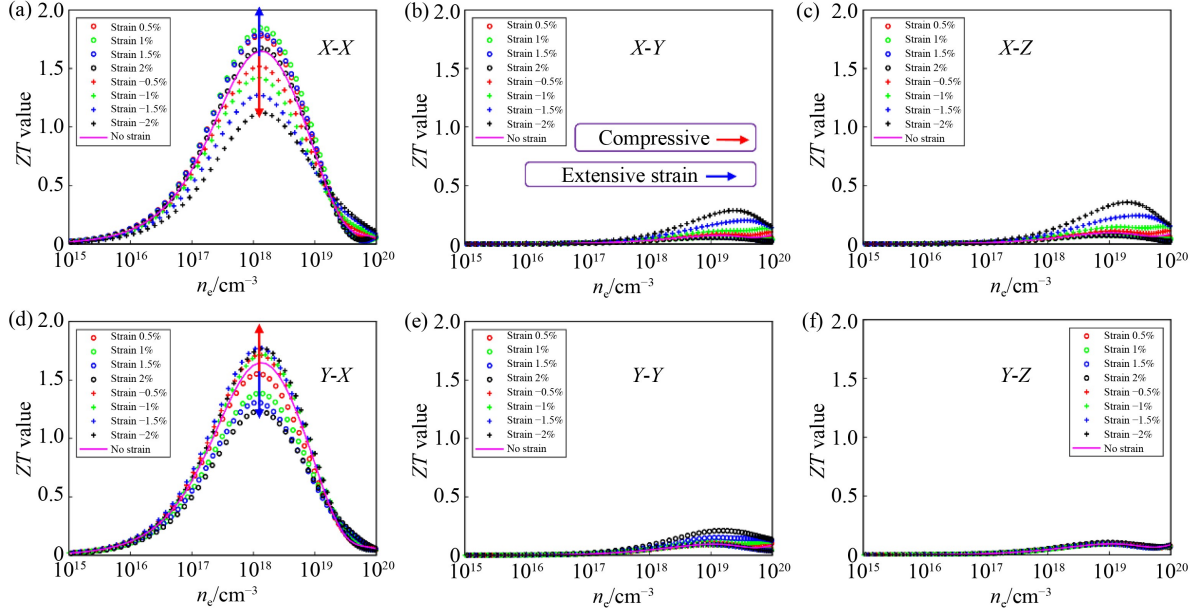


Fig. 8 Anisotropic ZT values of CsPbIBr₂ at 300 K under mechanical deformations.

(a–c) The anisotropic ZT values as a function of the carrier concentration n_e , when strain is applied along X direction; (d–f) the anisotropic ZT values as a function of the carrier concentration n_e , when strain is applied along Y direction. (Here the anisotropic ZT values for the Z - X (Y - Z , Z - Y) case were not shown, as they are similar to those for the Y - X (Y - Z , Y - Y) cases (see Fig. S17)).

thermoelectric device as a function of the hot-side temperatures coming from different heat sources (room temperature at the cold-side) was estimated. As shown in Fig. 9, the conversion efficiency is highly enhanced from CsPbI₃ ($ZT = 0.5$) to CsPbIBr₂ ($ZT = 1.85$) under intrinsic

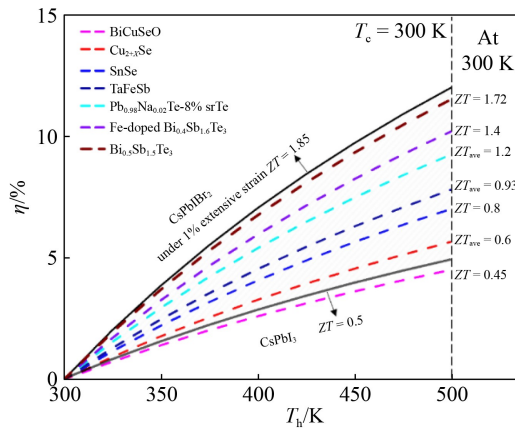


Fig. 9 Thermoelectric energy conversion efficiency of inorganic halide perovskites compared with other thermoelectric materials. (Efficiency of CsPbI₃ without strain, and CsPbIBr₂ under 1% extensive strain as a function of the hot-side temperature, compared with other experimental reports of other promising thermoelectric materials, including BiCuSeO ($ZT \sim 0.45$ at 300 K) [71], α -Cu_{2+x}Se (average $ZT \sim 0.6$ between 300 and 400 K) [72], SnSe ($ZT = 0.8$ at 300 K) [73], TaFeSb (average $ZT = 0.93$ between 300 and 973 K) [74], Pb_{0.98}Na_{0.02}Te-8%SrTe (average $ZT = 1.2$ between 300 and 800 K) [75], Fe-doped Bi_{0.4}Sb_{1.6}Te₃ ($ZT \sim 1.4$ at 300 K) [67], and Bi_{0.5}Sb_{1.5}Te₃ ($ZT = 1.72$ at 300 K) [68]).

strains and mechanical deformation, especially at high temperatures. Such high efficiency is comparable or even higher than many promising bulk thermoelectric materials [70], (besides the Bi₂Te₃ series) including the multicomponent oxides series, CuSe composites series, SnSe series, half-Heusler series, GeTe/PbTe series, and etc. Herein, one experimental report of the promising thermoelectric materials among each series is chosen as examples, such as BiCuSeO ($ZT \sim 0.45$ at 300 K) [71], α -Cu_{2+x}Se (experimental average $ZT \sim 0.6$ between 300 and 400 K) [72], SnSe ($ZT = 0.8$ at 300 K) [73], TaFeSb (average $ZT = 0.93$ between 300 and 973 K) [74], Pb_{0.98}Na_{0.02}Te-8%SrTe (average $ZT = 1.2$ between 300 and 800 K) [75]. The power generation efficiency can reach as high as 4.9% (CsPbI₃) to 12% (CsPbIBr₂ under 1% extensive strain) at 500 K, and these enhancements suggest that mechanical deformation in combination with the alloy engineering are efficient and controllable strategies, and the thermoelectric device with such high efficiency is promising to be applied in thermoelectrical fields and recycle the waste heat.

4 Conclusions

In summary, it is discovered in this paper that mechanical deformation can fine-tune electronic band structures, anisotropic thermoelectric transport properties, and ZT values of mixed halide perovskites CsPb(I_{1-x}Br_x)₃. While halide mixing can readily introduce splitting of the original three-fold degenerated Pb-6p orbitals in pure

halide perovskites (CsPbI_3 and CsPbBr_3) due to symmetry-breaking induced intrinsic strains, the shifts of these orbitals are highly anisotropic and challenging to control in various mixed halide perovskite polymorphs. In meeting this challenge, mechanical deformation can further push the orbital energies apart from each other in a more controllable manner, and therefore, the CBM can be effectively controlled through mechanical deformation, out-running the impact from the pre-existed intrinsic strains. For example, the directional dependent Pb-6p orbital energy levels would shift down with extensive strain or shift up with compressive strain. The resulting carrier effective mass would vary dramatically due to the reconstruction of the CBM, attributing to the downward shifted Pb-6p_x, 6p_y, or 6p_z orbital that replaces the original CBM orbital. The carrier effective masses would then correlate inversely with the carrier relaxation time to influence other electronic transport properties. As a result, the Seebeck coefficient decreases as the three-fold degenerated orbitals split, while the electric conductivity along a direction would increase at lower carrier concentrations, when the orbital energy level along that same direction decreases. More interestingly, the reduced Seebeck coefficient and increased electric conductivity result in a significant reduction of the optimal carrier concentration to achieve maximum ZT values, providing a new avenue to meet the longstanding challenges in doping perovskites at higher carrier concentrations. Finally, the thermoelectric energy conversion efficiency can be tailored from (CsPbI_3) 4.9% to 12% (CsPbIBr_2 under 1% extensive strain) under intrinsic strains and mechanical deformation at 500 K. It is believed that this paper will provide fundamental insights into the synergetic strategy to combine halogen mixing (symmetry-breaking) and mechanical deformation to enhance the thermoelectric performance and optimize the doping process in mixed halide perovskites.

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