Perspectives and Design Principles of Vacancy-Ordered Double Perovskite Halide Semiconductors

Annalise E. Maughan,[†] Alex M. Ganose,^{‡,¶,§} David O. Scanlon,^{‡,¶,§} and
James R. Neilson^{*,†}

[†]*Department of Chemistry, Colorado State University, Fort Collins, CO, 80523-1872*

[‡]*University College London, Kathleen Lonsdale Materials Chemistry, Department of Chemistry,
20 Gordon Street, London WC1H 0AJ, UK*

[¶]*Diamond Light Source Ltd., Diamond House, Harwell Science and Innovation Campus, Didcot,
Oxfordshire OX11 0DE, UK*

[§]*Thomas Young Centre, University College London, Gower Street, London WC1E 6BT, UK*

E-mail: james.neilson@colostate.edu

Abstract

Halide perovskite semiconductors such as methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) have achieved great success in photovoltaic devices, yet concerns surrounding toxicity of lead and material stability have motivated the field to pursue alternative perovskite compositions and structures. Vacancy-ordered double perovskites are a defect-ordered variant of the perovskite structure characterized by an antiferro arrangement of isolated octahedral units bridged by A-site cations. In this perspective, we focus upon the structure-dynamics-property relationships in vacancy-ordered double perovskite semiconductors as they pertain to applications in photovoltaics, and propose avenues of future study within the context of the broader

perovskite halide literature. We describe the compositional and structural motifs that dictate the optical gaps and charge transport behavior and discuss the implications of charge ordering, lattice dynamics, and organic-inorganic coupling upon the properties of these materials. The design principles we elucidate here represent a first step towards extending our understanding of perovskite functionality to defect-ordered perovskites.

Introduction

Perovskite halide semiconductors have taken the materials science and solid-state chemistry communities by storm, owing to their compositional and structural diversity that enables a wide array of functional properties. In particular, photovoltaic devices containing the hybrid perovskite methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) have demonstrated photoconversion efficiencies up to 22%.¹ However, given the concerns regarding toxicity and stability of $\text{CH}_3\text{NH}_3\text{PbI}_3$,^{2,3} alternative compositional and structural derivatives of the perovskite family, including layered Ruddlesden-Popper perovskites⁴ and ordered double perovskites (*i.e.* $\text{Cs}_2\text{AgBiI}_6$),^{5,6} have been recently explored to assess their potential in photovoltaic applications. In the present perspective, we direct our focus on the family of perovskite derivatives called vacancy-ordered double perovskites, which are a structural derivative of the archetypal perovskite structure. The structure is derived from the conventional perovskite by doubling the ABX_3 unit cell along all three crystallographic axes and then removing every-other B -site cation, as illustrated in the schematic in Figure 1. The structure can alternatively be thought of as an antiferro arrangement of A -site cations and anionic $[BX_6]$ units, to which these materials are often referred.

While prior literature of the vacancy-ordered double perovskites focused almost exclusively upon their structural and dynamic behavior, the properties of these materials relevant to potential applications in perovskite photovoltaics have only recently been explored. Rekindled interest in the vacancy-ordered double perovskite family was motivated by a study by Lee *et al.* in 2014, which demonstrated that cesium tin(IV) iodide (Cs_2SnI_6) exhibits optical and electronic properties relevant for applications in photovoltaics.⁷ Cs_2SnI_6 possesses a direct optical gap of 1.3 eV,

Figure 1: A schematic of the relationship between the archetypal perovskite (ABX_3) and vacancy-ordered double perovskite (A_2BX_6) structures.

corresponding to its deep black color.^{7,8} Electrical resistivity measurements indicate that Cs_2SnI_6 is a native n -type semiconductor with a moderate electron mobility of $310 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is of the same order of magnitude as the value of $585 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ reported for CsSnI_3 , despite the presence of ordered vacancies in Cs_2SnI_6 .⁹ Lee *et al.* demonstrated that p -type conductivity could be achieved under appropriate doping conditions, though the hole mobilities ($42 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) were notably lower than the electron mobilities.⁷ A computational study of the defect chemistry in Cs_2SnI_6 suggested that the ambipolar doping and charge transport in Cs_2SnI_6 was due to the formation of n -type iodide vacancies/tin interstitials or p -type cesium vacancies.¹⁰ Despite the lower hole mobilities, a dye-sensitized solar cell utilizing Cs_2SnI_6 as a hole-transporting material was reported to achieve 7.8% power conversion efficiency.⁷ The presence of formally tetravalent tin in Cs_2SnI_6 is suggested to improve air and moisture stability relative to the Pb^{2+} - and Sn^{2+} -based ABX_3 perovskites, as well as mitigate toxicity concerns associated with the use of lead. The advantageous properties of Cs_2SnI_6 motivates further study of the structure-property relationships in vacancy-ordered double perovskites for potential optoelectronic applications.

This perspective brings together our understanding of the structure-dynamics-property relationships in vacancy-ordered double perovskite halide semiconductors. We focus our attention on recent experimental and computational studies and construct a set of guiding principles to explain and predict the optical and electronic properties of vacancy-ordered double perovskites with relevance for potential applications in photovoltaics.

Optical Gap and Band Alignment

The band gap and optical absorption of vacancy-ordered double perovskites is dictated by the electronic states of the *B*- and *X*-site ions. We first consider the impact of the *X*-site halogen upon the band alignment and optical gap. Incorporation of smaller halogens across the series $\text{I}^- \rightarrow \text{Br}^- \rightarrow \text{Cl}^-$ results in a progressive widening of the band gap, as illustrated in a computational study by Cai *et al.*¹¹ As shown in Figure 2, the calculated band gaps of the iodide-based vacancy-ordered double perovskites are, in general, smaller than those of the bromide and chloride analogs, and the band gaps increase monotonically within a compositional family in which the *A*- and *B*-site cations are unchanged. This notion is evidenced by the trend in experimentally-determined optical gaps for the Cs_2SnX_6 and Cs_2TiX_6 series. Cs_2SnI_6 is reported to exhibit an experimental optical gap of ~ 1.3 eV,^{7,12–14} yet replacing I^- with Br^- and Cl^- increases the optical gap to 2.7 eV and 3.9 eV, respectively.^{12,15} Similarly, Cs_2TiI_6 exhibits an optical gap of 1.02 eV while a larger optical gap of 1.78 eV is observed for Cs_2TiBr_6 .¹⁶ This trend is conserved across all members of the vacancy-ordered double perovskite family for a given combination of *A*- and *B*-site cations.

Figure 2: DFT-calculated band gaps of the A_2BX_6 compounds in which the *A*-, *B*-, and *X*-sites were systematically varied. Figure reproduced with permission from Cai, Xie, Ding, Chen, Thirumal, Wong, Mathews, Mhaisalkar, Sherburne, Asta, *Chem. Mater.*, **2017**, 29, 7740–7749.¹¹

The impact of the *X*-site upon the optical gap stems from the strong presence of halogen states at the valence and conduction band edges. In most members of the vacancy-ordered double per-

ovskite family, the valence band maximum (VBM) is derived exclusively from the halogen p states, and thus the energy of the valence band is dictated predominantly by the choice of halogen. This notion is exemplified by the Cs_2SnX_6 series ($X = \text{I}^-$, Br^- , Cl^-) and is illustrated through simplified molecular orbital diagrams of the Sn–X interactions within the octahedra. As shown in Figure 3, the highest occupied states are derived from the halogen non-bonding p states. Upon incorporation of the smaller halides, these states move to lower energies as the ionization potential of the halogen p orbitals decreases across the $\text{I}^- \rightarrow \text{Br}^- \rightarrow \text{Cl}^-$ series, resulting in a widening of the optical gap observed experimentally.¹² Substitution at the X-site has been employed to tune the band gap in the mixed halide series $\text{Cs}_2\text{SnI}_{6-x}\text{Br}_x$ and $\text{Cs}_2\text{TiI}_{6-x}\text{Br}_x$, though the optical gaps do not change linearly with respect to halide concentration.^{15,16}

Figure 3: Molecular orbital theory perspective of the frontier states of (a) Cs_2SnI_6 , (b) Cs_2SnBr_6 , and (c) Cs_2SnCl_6 considering the interactions between the Sn and I orbitals.

The X-site anion further contributes to the band gap through interactions with the B-site cation at the center of the octahedra to dictate the energy of the conduction band minimum. In the Cs_2SnX_6 series, the conduction band minimum is derived from hybridized Sn 5s and X p states,^{7,12,13,17,18} as predicted by the molecular orbital theory diagram in Figure 3. As the halogen p states fall closer in energy to the Sn 5s states, the energy of the lowest unoccupied states is pushed higher in energy as their interaction becomes more covalent. The increase in band gap for the smaller halogens is

therefore due to a combination of the valence band moving to lower energies with an increase in energy of the conduction band minimum. It has been noted recently that the proportional change in band gap across the Cs_2SnX_6 ($X = \text{I}^-$, Br^- , Cl^-) series is significantly larger than is observed for the CsSnX_3 perovskites.¹⁹ In CsSnX_3 , the calculated band gaps lie between $E_g = 1.3\text{--}2.7$ eV from $X = \text{I}^- \rightarrow \text{Br}^- \rightarrow \text{Cl}^-$ for the cubic $Pm\bar{3}m$ perovskite phase,²⁰ while the band gaps in Cs_2SnX_6 span a much larger range from $E_g = 1.3\text{--}3.9$ eV.^{12,19} In the CsSnX_3 series, the formally filled Sn 5s orbitals result in a valence band maximum derived from hybridized Sn 5s/halogen p states, while the conduction band minimum is derived from hybridized Sn 5p/halogen p states.²⁰ Due to the hybridization of the Sn/halogen states at the valence band maximum, incorporation of smaller halogens with lower ionization potentials depresses the valence band energy only slightly. In contrast, the valence band maxima of the Cs_2SnX_6 vacancy-ordered double perovskites are derived from the non-bonding halogen states, and thus the valence band maximum is depressed concomitantly with the ionization potential of the halogen. This results in a significant widening and larger proportional increase of the band gap upon incorporation of smaller halogens in the Cs_2SnX_6 vacancy-ordered double perovskites compared to the CsSnX_3 compounds. As most vacancy-ordered double perovskites exhibit similar orbital character at the valence and conduction band edges, the molecular orbital theory diagrams shown in Figure 3 serve as a simple predictive tool to understand the influence of B - and X -site substitution upon the band gap.

The trends in band gap reported in the literature and predicted by the molecular orbital theory perspective shown in Figure 3 are further supported by the reported band alignments of several members of the vacancy-ordered double perovskite family. As shown in Figure 4, the ionization potentials for the bromide-based vacancy-ordered double perovskites lie at lower energies than their iodide analogs. For example, the experimental ionization potentials for Cs_2SnI_6 range from -5.42 eV to -5.94 eV and the electron affinities range from -4.12 eV to -4.95 eV for polycrystalline samples.^{7,13,15,21} In contrast, the ionization potential of polycrystalline Cs_2SnBr_6 falls deeper in energy at -6.62 eV, and the electron affinity is pushed higher in energy to reside at -3.77 eV, consistent with the large increase in band gap.¹⁵ A similar observation is expected for

Cs_2SnCl_6 , though photoelectron spectroscopy studies are likely complicated by its high electrical resistivity.¹²

Figure 4: Comparison of the experimentally- and computationally-determined ionization potentials and electron affinities of several members of the vacancy-ordered double perovskite family. Dashed lines represent the reported Fermi levels. Values were taken from (a),¹⁵ (b),⁷ (c),¹³ (d),²¹ (e),²² (f),²³ (g),¹⁵ (h),¹⁵ (i),¹⁵ (j),¹⁵ (k),¹⁵ (l),²⁴ (m),¹³ (n),¹⁸ (o),¹⁸ (p),¹⁸ (q).¹³

While both conduction and valence band edges exhibit character from the halogen p states, deviations in the close-packing of the halogen sublattice do not appear to strongly influence the optical gap and band alignment in the vacancy-ordered double perovskites. In Rb_2SnI_6 , the smaller size of the Rb^+ ion yields a tetragonal variant of the vacancy-ordered double perovskite structure characterized by cooperative octahedral tilting, and it further undergoes a phase transition to a monoclinic structure with additional tilting motifs.¹⁸ Tetragonal Rb_2SnI_6 exhibits an optical gap of 1.32(2) eV, which is only slightly higher than the value of 1.23(3) eV determined for Cs_2SnI_6 by the same method. This observation is further mirrored in the DFT-calculated band alignments. Despite the lower-symmetry structure, the valence band maxima of both cubic Cs_2SnI_6 and tetragonal

Rb₂SnI₆ are calculated to reside at -5.8 eV (Figure 4). The electron affinity of Rb₂SnI₆ (-4.7 eV) moves to slightly higher energy than that of Cs₂SnI₆ (-4.8 eV), likely responsible for the slight increase in optical gap observed experimentally. The band alignments of the monoclinic variant are also relatively unchanged. Taken together, these observations suggest that cooperative octahedral tilting does not strongly affect the optical absorption behavior or electronic structure of vacancy-ordered double perovskite semiconductors. Rather, the optical absorption can be considered as a metal to metal/ligand charge transfer process within the [BX₆] octahedra, lending further credence to the predictive capability of the molecular orbital theory approach.

The interaction of the *B*-site with the halide ligands of the octahedra dictates the magnitude of and direct vs. indirect nature of the band gap. While Cs₂SnI₆ possesses a direct band gap of ~ 1.3 eV,^{7,12–14} replacing Sn with Te at the *B*-site yields a larger, indirect band gap of 1.59 eV for Cs₂TeI₆.¹³ The larger magnitude of the band gap in Cs₂TeI₆ arises due to covalent interaction of the Te 5*p* states with the I 5*p* states that pushes the conduction band higher in energy, as shown in the molecular orbital diagram in Figure 5. As the valence band is pinned at the iodine 5*p* states that dominate the valence band, the band gap is determined exclusively by the energy of the Te/I states at the conduction band minimum. Consideration of the orbital symmetry and character enables prediction of the direct vs. indirect nature of the band gaps in Cs₂SnI₆ and Cs₂TeI₆. From the molecular orbital theory perspective of the Sn–I interactions within an [SnI₆] octahedron, the highest occupied states of Cs₂SnI₆ are derived from a triply degenerate *T*_{1*g*} I 5*p* orbital set, while the lowest unoccupied state is *A*_{1*g*} character derived from the Sn 5*s*/I 5*p* orbitals (Figure 5a). By considering the interactions of the *T*_{1*g*} I 5*p* orbital set between octahedra, the highest energy state occurs when these orbitals are out of phase with those of the neighboring octahedra at the Γ point. At the conduction band minimum, the lowest energy state occurs at the Γ point and corresponds to in-phase interactions between the *A*_{1*g*} orbitals, as shown in Figure 6. This produces a direct band gap at the Γ point. In Cs₂TeI₆, the valence band maximum is derived predominantly from the *T*_{1*g*} I 5*p* orbital set, similarly to that observed for Cs₂SnI₆. We note that the reported band structure for Cs₂TeI₆ exhibits a small contribution from the Te 5*s* states, however the valence

band is overwhelmingly I 5*p* character by comparison, and our calculations have shown that the ordering of the orbitals is quite sensitive to the choice of exchange correlation functional.^(CITE) The conduction band minimum is derived of a triply degenerate T_{1u} orbital set derived from Te 5*p* and I 5*p* states. As the frontier states of Cs_2TeI_6 are both composed of states with *p* orbital symmetry, the nature of the band gap is necessarily indirect, occurring between the L and X points in the Brillouin zone.

Figure 5: Molecular orbital theory perspective of the frontier states of (a) Cs_2SnI_6 and (b) Cs_2TeI_6 with orbital representations of the highest occupied and lowest unoccupied states of $[\text{SnI}_6]$ and $[\text{TeI}_6]$ octahedra calculated using GAMESS.

Consideration of the orbital character at the band edges provides insight into the nature of the band gap of the transition-metal-based vacancy-ordered double perovskites. In these compounds, the halogen *p* states comprise the valence band maximum while the *d* states of the Ti(IV), Pd(IV), or Pt(IV) ions comprise the conduction band minimum. In the Cs_2TiX_6 system, the conduction band is derived predominantly from fairly localized Ti 3*d* states, with a small contribution from the halogen *p* states near the conduction band edge, resulting in an indirect band gap.¹⁶ Similarly to Cs_2SnI_6 , the highest occupied states in Cs_2PdBr_6 are derived from the Br 4*p* orbitals to yield a triply degenerate orbital set with the highest energy state at the Γ point.²⁴ The conduction band

is composed of Pd 4*d* and Br 4*p* states. A 3D projection of the wavefunction distribution at the conduction band minimum of Cs₂PdBr₆ indicate that the lowest unoccupied state is composed of hybridized Pd *d_z²* and Br 4*p* orbitals within the octahedra occurring at the X point in the Brillouin zone, presumably due to lower-energy in phase interactions between neighboring octahedra. This orbital configuration produces an indirect band gap between the Γ and X points of the Brillouin zone. The vacancy-ordered double perovskite (NH₄)₂PtI₆ is also reported to exhibit an indirect band gap of ~ 2 eV arising from transitions between I 5*p* character at the Γ point to the Pt 5*d e_g* states at X.²⁵ The reported optical gaps of other members of the hybrid Pt–I family are included in Table 1 for comparison, though only (NH₄)₂PtI₆ crystallizes in the cubic vacancy-ordered double perovskite structure.²⁵ A table of experimentally-determined optical gaps and the direct vs. indirect nature of the band gap of several members of the vacancy-ordered double perovskite family compiled in Table 1.

Figure 6: Band structure of Cs₂SnI₆, highlighting the *A*_{1g} antibonding states. Simplified bonding diagram (a and d) and charge density isosurfaces (c and e) of the highlighted band at the Γ and X points. The isosurface level was set to 0.008 eV Å⁻³. Figure reproduced with permission from A. M. Ganose Copyright 2018 University of College London.²⁶

It is important to note that the fundamental band gap, determined as the energy gap between the valence band maximum and conduction band minimum, is not necessarily reflective of the true *optical gap* or *absorption onset* observed by absorption spectroscopy in some members of the

vacancy-ordered double perovskite family. In the $A_2\text{SnI}_6$ ($A = \text{Rb}^+, \text{Cs}^+, \text{CH}_3\text{NH}_3^+, \text{CH}(\text{NH}_2)_2^+$) series, the direct transition at the Γ point is dipole-forbidden, and thus the dominant optical absorption occurs from states slightly below the valence band edge.^{13,17,18} Similarly, the indirect band gap of Cs_2PdBr_6 from Γ -X is dipole-forbidden, though Sakai *et al.* note that transitions become allowed by moving slightly away from the X point.²⁴ The presence of disallowed transitions at the fundamental gap results in significant discrepancies between the calculated band gap and the experimental optical gap in these materials. As such, computational studies of these materials may also invoke an artificially large amount of Hartree-Fock exchange to fit the fundamental band gap to the experimentally observed optical gap.^{8,10,22} For Cs_2SnI_6 , the calculated band gap from GW0 calculations predict a band gap of ~ 0.88 eV,^{12,13} though the optical gap determined by UV-visible diffuse reflectance spectroscopy is nearly 0.5 eV larger at ~ 1.3 eV.^{7,12–14} The optical gaps of Cs_2SnBr_6 (2.7 eV) and Cs_2SnCl_6 (3.9 eV) are also underestimated by the GW0 calculated band gaps of 2.241 eV and 3.226 eV, respectively,¹² suggesting that the direct fundamental band gap is also dipole-disallowed in these materials; this observation likely stems from the fact that the electronic structures of the Cs_2SnX_6 are derived of nearly identical orbital character and symmetry at both the valence and conduction band edges.¹²

One finds discussion in the literature regarding the true valence state of the Sn ions in Cs_2SnI_6 . Formal oxidation state and electron counting yields tetravalent Sn with an electron configuration of $[\text{Kr}]5s^05p^0$. A computational study by Xiao *et al.* proposed that the true valence state of the Sn ion is divalent as in CsSnI_3 rather than tetravalent due to population of the Sn 5s states.¹⁰ A more recent combined experimental and computational study demonstrated that the loss of two electrons (addition of two holes) upon oxidation of Sn^{2+} to Sn^{4+} from CsSnX_3 to Cs_2SnX_6 is accompanied by a renormalization of the hybridized Sn 5s and X *p* orbitals that redistributes the charge over the Sn–X bond, rather than localizing holes in the Sn orbitals.¹⁹ This effect occurs due to covalency between the tin and halide ions, and is therefore predicted to occur to a much lesser extent in members of the Cs_2SnX_6 series with strongly ionic interactions (*e.g.*, the hypothetical Cs_2SnF_6). While the covalent nature of the Sn–I interactions may result in changes to the electron density

within the octahedra, formal oxidation states and electron counting provides an excellent predictor of the orbital character of the valence and conduction bands, and the nature and magnitude of the band gap, as illustrated in Figure 3 and Figure 5.

Table 1: Experimentally-determined optical gaps of several vacancy-ordered double perovskite halide semiconductors.

Compound	Optical gap (eV)	Direct/Indirect	Reference
Cs ₂ SnI ₆	1.26	direct	7
Cs ₂ SnI ₆	1.25	direct	13
Cs ₂ SnI ₆ (thin film)	1.62	direct	22
Cs ₂ SnI ₅ Br	1.38	direct	15
Cs ₂ SnI ₄ Br ₂	1.40	direct	15
Cs ₂ SnI ₃ Br ₃	1.43	direct	27
Cs ₂ SnI ₂ Br ₄	1.63	direct	15
Cs ₂ SnIBr ₅	2.3	direct	15
Cs ₂ SnBr ₆	2.7	direct	12
Cs ₂ SnBr ₆	2.9	direct	15
Cs ₂ SnCl ₆	3.9	direct	12
Cs ₂ PdBr ₆	1.6	indirect	24
(NH ₄) ₂ PtI ₆	~2	indirect	25
(CH ₃ NH ₃) ₂ PtI ₆ *non-VODP	~2	indirect	25
(CH(NH ₂) ₂) ₂ PtI ₆	~2	indirect	25
(C(NH ₂) ₃) ₂ PtI ₆ *non-VODP	~2	indirect	25
Cs ₂ TiI ₆	1.02	indirect	16
Cs ₂ TiI ₄ Br ₂	1.15	indirect	16
Cs ₂ TiI ₂ Br ₄	1.38	indirect	16
Cs ₂ TiBr ₆	1.78	indirect	16,28
Cs ₂ TeI ₆	1.59	indirect	13
Rb ₂ SnI ₆	1.32(2)	direct	18
(CH ₃ NH ₃) ₂ SnI ₆	1.35(2)	direct	17
(CH ₃ NH ₃) ₂ SnI ₆ (thin film)	1.81	direct	23
(CH(NH ₂) ₂) ₂ SnI ₆	1.37(2)	direct	17

Electronic Dispersion and Charge Transport

Due to the absence of extended polyhedral connectivity between the [BX₆] octahedra, vacancy-ordered double perovskites are often referred to as “zero-dimensional” perovskite derivatives. However, this name is misleading, as it implies that the octahedra are isolated electronically

from one another. Rather, vacancy-ordered double perovskites retain a close-packed framework of halides familiar to ABX_3 perovskites that can engage in orbital overlap with neighboring octahedra to produce dispersive electronic states. It is therefore important to consider the *electronic dimensionality*, rather than structural dimensionality, when deriving structure-property relationships in these materials.²⁹

As the valence band of vacancy-ordered double perovskites is derived predominantly from the halogen p states, the electronic dispersion of the valence band and thus the hole effective masses and transport are dictated by the orbital overlap within the close-packed halide framework. As such, replacing the larger iodide with bromide is accompanied by an increase in the hole effective mass due to reduced overlap between the smaller orbitals of the bromide sublattice. This notion is demonstrated by comparison of the cubic vacancy-ordered double perovskites Cs_2TiI_6 and Cs_2TiBr_6 and Cs_2PdI_6 and Cs_2PdBr_6 . The calculated hole effective masses of Cs_2TiI_6 range from $0.79\text{--}1.58m_0$, yet replacing iodide with bromide increases the hole effective masses to $0.9\text{--}1.79m_0$.¹⁶ Similarly, Cs_2PdI_6 exhibits a hole effective mass of $0.85m_0$ ¹¹ while a larger hole effective mass of $1.37m_0$ is reported for Cs_2PdBr_6 .²⁴ The impact of halogen substitution on both the electron and hole effective masses speaks to the prominence of the close-packed halide framework in dictating the charge transport behavior in vacancy-ordered double perovskites.

The dispersive conduction band states in Cs_2SnI_6 and other vacancy-ordered double perovskites are further dictated by interactions of the hybridized B - and X -site states between neighboring octahedra. To illustrate this point, we have calculated charge density isosurfaces of the lowest conduction band of Cs_2SnI_6 (Figure 6), at the Γ and X points in the Brillouin zone. At the Γ point, the A_{1g} antibonding orbital is in phase with the A_{1g} orbital in the adjacent cell (Figure 6b), leading to a bonding interaction between neighboring octahedra (Figure 6c). This interaction occurs across a distance of $\sim 4 \text{ \AA}$ between octahedra, due to the disperse projection of the iodine $5p$ orbitals into the interoctahedral void and acts to stabilize the bonding at this k -point. In contrast, at the X point, the A_{1g} antibonding orbital is out of phase with the A_{1g} orbital in the adjacent cell (Figure 6d), resulting in an antibonding interaction between neighboring octahedra (Figure 6e).²⁶ As such, the

energy of the interaction at the X point is significantly higher, giving rise to reasonably high band dispersion. The large conduction band dispersion of Cs_2SnI_6 leads to calculated electron effective masses as low as $0.25m_0$.¹⁷ A similar argument can be made for the dispersive conduction band of Cs_2TeI_6 by considering the interaction of the triply degenerate T_{1u} orbital sets between octahedra that produces electron effective masses ranging from $0.22m_0$ to $0.97m_0$.^{11,13}

Similarly to the main-group metal-halide vacancy-ordered double perovskites, the palladium and platinum-based vacancy-ordered double perovskites $(\text{NH}_4)_2\text{PtI}_6$ and Cs_2PdBr_6 exhibit dispersive conduction bands and relatively low electron effective masses.^{24,25} In Cs_2PdBr_6 , the conduction band minimum is derived from a hybridized electronic state of the Pd $4d z^2$ orbitals with the Br $4p$ orbitals.²⁴ The relatively low electron effective mass of $0.53m_0$ is therefore determined by the overlap of these hybridized states with those of the neighboring octahedra. In contrast, the conduction band minimum of $(\text{NH}_4)_2\text{PtI}_6$ is comprised of only the Pt $5d e_g$ orbital set with little or no contribution from the iodine p states, which produces electron effective masses ranging from 0.38 - $0.43m_0$.²⁵ While the Pd- and Pt-based vacancy-ordered double perovskites exhibit fairly dispersive conduction band states, the analogous electron-poor Ti-based compounds exhibit significantly more localized states in the conduction band.¹⁶ In Cs_2TiX_6 , the conduction band minimum is derived from the Ti $3d$ states. These localized conduction band states resulting in large electron effective masses of $1.58m_0$ and $1.79m_0$ for Cs_2TiI_6 and Cs_2TiBr_6 , respectively. On the other hand, electronic dispersion from the close-packed halogen lattice produces lighter hole effective masses. As such, Cs_2TiI_6 and Cs_2TiBr_6 are the only compounds of those considered here that are expected to exhibit higher hole mobilities than electron mobilities. The reduced dispersion in Cs_2TiX_6 compared to Cs_2PdBr_6 and $(\text{NH}_4)_2\text{PtI}_6$ may be due to the larger size of the $4d$ and $5d$ orbitals of Pd and Pt that can engage in stronger orbital overlap between neighboring octahedra compared to the smaller spatial distribution of the Ti $3d$ orbitals. The calculated electron and hole effective masses for several members of the vacancy-ordered double perovskite family are provided in Table 2.

Table 2: Calculated electron and hole effective masses for several members of the vacancy-ordered double perovskite family given in units of m_0 .

Compound	Spacegroup	m_e^*	m_h^*	Reference
Cs ₂ SnI ₆	$Fm\bar{3}m$	0.25	0.81	17
Cs ₂ SnI ₆	$Fm\bar{3}m$	0.33	1.5	11
Cs ₂ SnI ₆	$Fm\bar{3}m$	0.48-0.92	1.32-2.75	13
(CH ₃ NH ₃) ₂ SnI ₆	$Fm\bar{3}m$	0.31	0.99	17
(CH(NH ₂) ₂) ₂ SnI ₆	$Fm\bar{3}m$	0.43	1.61	17
(NH ₄) ₂ PtI ₆	$Fm\bar{3}m$	0.38-0.43	0.64-25.3	25
Cs ₂ TeI ₆	$Fm\bar{3}m$	0.40	1.51	11
Cs ₂ TeI ₆	$Fm\bar{3}m$	0.22-0.97	1.40-4.40	13
Cs ₂ TiI ₆	$Fm\bar{3}m$	1.58	0.79-1.58	16
Cs ₂ TiBr ₆	$Fm\bar{3}m$	1.79	0.9-1.79	16
Cs ₂ PtI ₆	$Fm\bar{3}m$	0.51	1.45	11
Cs ₂ PdI ₆	$Fm\bar{3}m$	0.47	1.37	11
Cs ₂ PdBr ₆	$Fm\bar{3}m$	0.53	0.85, 19.9	24
Rb ₂ PtI ₆	$P4/mnc$	0.59-0.66	1.32-2.5	11
K ₂ PtI ₆	$P4/mnc$	0.83-0.84	1.79-2.55	11
Rb ₂ SnI ₆	$P4/mnc$	0.39	0.98	18
Rb ₂ SnI ₆	$P4/mnc$	0.65	2.17-2.61	11
Rb ₂ SnI ₆	$P2_1/n$	0.44	1.07	18
(CH(NH ₂) ₂) ₂ PtI ₆	$P2_1/n$	0.61-0.87	1.74-1.75	25
(CH ₃ NH ₃) ₂ PtI ₆ *nonVODP	$R\bar{3}m$	0.61-0.74	1.29-2.30	25
(CH(NH ₂) ₃) ₂ PtI ₆ *nonVODP	$P6_3/mmc$	2.05-32.2	3.19-6.08	25

Defect Chemistry

The chemistry of the B -site cation plays a non-trivial role in dictating the defect behavior of vacancy-ordered double perovskites. Cs₂SnI₆ exhibits native n -type conductivity, with free electrons generated by the formation of iodine vacancy defects that form as donor states that are nearly resonant with the conduction band.^{7,8,13} The lack of trap-state defects classify Cs₂SnI₆ as a defect-tolerant semiconductor.¹³ Other members of the A_2 SnI₆ ($A = \text{Rb}^+, \text{Cs}^+, \text{CH}_3\text{NH}_3^+, \text{CH}(\text{NH}_2)_2^+$) series exhibit native n -type conductivity, presumably due to similar defect chemistry arising from their analogous electronic structures.^{17,18} Yet, replacing Sn⁴⁺ with Te⁴⁺ significantly impacts the defect chemistry and charge transport behavior in the Cs₂Sn_{1-x}Te_xI₆ series. While iodine vacancies exhibit the lowest enthalpy of formation in both Cs₂SnI₆ and Cs₂TeI₆, replacing Sn with

Te increases the enthalpy of formation by a factor of $\sim 2-4$, which accounts for the exponential decrease in carrier concentration observed experimentally.¹³ Further, hybridization of the Te $5p$ and I $5p$ states pushes the conduction band minimum higher in energy, such that the iodine vacancy defect states reside as trap states deep within the band gap, which are proposed to localize charge carriers and inhibit charge transport.¹³ The defect tolerance vs. intolerance is attributed to the differences in electronic structure brought about by the Sn–I/Te–I hybridization at the conduction band and the increased covalency of the Te–I bonds that results in higher enthalpies of defect formation in Cs_2TeI_6 relative to Cs_2SnI_6 .

In contrast to defect-tolerant Cs_2SnI_6 , Cs_2TiI_6 appears to be intolerant to the formation of defects. Defect calculations of Cs_2TiI_6 indicate that, under I-rich and Ti-lean conditions, iodine vacancies are the lowest enthalpy of formation defect. Under I-lean/Ti-rich conditions, Cs_i and Ti_i are the lowest enthalpy of formation defects. However, these defect states form deep within the band gap and may therefore act as a recombination center for photoexcited charge carriers. The apparent defect intolerance of Cs_2TiI_6 may be rationalized by considering the bonding vs. antibonding orbital contributions at the valence and conduction band edges. The valence band appears to be derived from non-bonding I $5p$ states, while the conduction band minimum is derived from Ti–I antibonding character. Semiconductors with antibonding states at the conduction band minimum have been previously identified as defect intolerant by Zakutayev *et al.*, as the defect electronic states form as deep trap states rather than as resonances within the band edges.³⁰ Thus, defects such as iodine vacancies in Cs_2TiI_6 are likely to form as deep trap states, rendering this material intolerant to defect formation.

Mixed Valence

Mixed-valence compounds in vacancy-ordered double perovskites occur through charge disproportionation of the formally tetravalent B -site cation into B^{3+} and B^{5+} species. In the Cs_2SbX_6 system ($X = \text{Cl}^-$, Br^-), the antimony ions at the B -site are disproportionated into Sb(III) and Sb(V) at the

center of the octahedra,^{31,32} as shown in the crystal structure model in Figure 7. Supercell ordering of Sb^{3+}X_6 and Sb^{5+}X_6 result in a tetragonal unit cell (space group $I4_1/amd$) rather than the cubic $Fm\bar{3}m$ K_2PtCl_6 structure.^{33–35} In contrast to the O_h symmetry of the octahedra in K_2PtCl_6 , the $[\text{SbX}_6]$ octahedra in these compounds are slightly distorted to D_{2d} symmetry, resulting in two long apical Sb–X bonds and four short equatorial Sb–X bonds.³⁵ These compounds are unique from other vacancy-ordered double perovskite halides in that their optical absorption arises due to a strong charge transfer band from the populated $5s$ states of the Sb^{3+} centers into the empty $5s$ states of the adjacent Sb^{5+} center, likely mediated by the halide ligands.^{32,36} In A_2SbCl_6 , this gives rise to a deep blue-purple coloration, while a deep black coloration is observed in A_2SbBr_6 .^{32,33,36} These charge transfer processes are intimately linked with the vibrational properties of these mixed valence materials.^{37–39} In a study by Clark and Swanson, low-temperature far infrared spectra of Cs_2SbCl_6 reveal sharp features corresponding to internal modes of the $[\text{SbCl}_6]$ octahedra.³⁸ At higher temperatures, these features are dampened and broadened concomitantly with the onset of thermally-activated charge transfer, indicating that the lattice dynamics are strongly perturbed by the electron transfer processes in these materials.

Figure 7: Crystal structure representation of $\text{Cs}_2\text{Sb}_{0.5}^{\text{III}}\text{Sb}_{0.5}^{\text{V}}\text{X}_6$ in the charge ordered tetragonal structure. The isolated and ordered $[\text{Sb}^{3+}\text{X}_6]$ and $[\text{Sb}^{5+}\text{X}_6]$ octahedra are differentiated as blue and red, respectively. Cesium ions are shown in grey and the X-site anions are shown in orange.

The antimony centers in the mixed-valence vacancy-ordered double perovskites may be sub-

stituted with other trivalent or tetravalent metal cations to elicit changes in the optical absorption and carrier transport properties of these compounds. A common substitution is of Sn(IV) as in the series $A_2\text{Sb}_{1-x}\text{Sn}_x\text{Cl}_6$ ($A = \text{Cs}^+, \text{NH}_4^+$), where tetravalent tin is randomly distributed over both Sb(III) and Sb(V) sites within the crystalline lattice.^{40,41} Substitution of Sn(IV) is found to dramatically decrease the intensity of the charge-transfer band by UV-visible spectroscopy due to dilution of the $\text{Sb}^{3+}\text{-Sb}^{5+}$ sublattice.⁴⁰ Higher tin concentrations are also accompanied by a reduction in electrical conductivity due to discontinuity of the Sb sublattice through which mobile holes travel via a thermally-activated hopping process.^{40,41} At Sb concentrations below 10%, the sign of the carriers changes from positive to negative, and the mechanism of charge transport is suggested to transition from electronic to ionic.⁴¹ Trivalent metal substitution for Sb^{3+} can drive both ordered and disordered configurations of the B^{3+} and Sb^{5+} sites.³⁵ For example, $\text{Cs}_2\text{In}_{0.5}^{\text{III}}\text{Sb}_{0.5}^{\text{V}}\text{Cl}_6$ exhibits disordered In^{III} and Sb^{5+} centers consistent with space group $Fm\bar{3}m$, with no evidence of ordering or phase transitions down to $T = 4.2$ K. In contrast, $\text{Cs}_2\text{Bi}_{0.5}^{\text{III}}\text{Sb}_{0.5}^{\text{V}}\text{Cl}_6$ adopts the tetragonal $I4_1/amd$ structure characterized by charge-ordered Bi^{III} and Sb^{5+} centers (Figure 7). The differences between ordered and disordered B -sites is attributed to the size of the B^{3+} cation; when the $[B^{3+}X_6]$ and $[\text{Sb}^{5+}X_6]$ octahedra are close in size, no supercell ordering is observed, while deviations in the octahedral sizes are accompanied by the presence of supercell reflections in the neutron powder diffraction data. Similarly to the ordered $\text{Cs}_2\text{Sb}_{1-x}\text{Sn}_x\text{Cl}_6$ series, the disordered $\text{Cs}_2\text{Sb}_{1-x}\text{In}_x\text{Cl}_6$ series exhibits a composition-dependent charge-transfer band in the UV-visible spectroscopic data, suggesting that the arrangement of the B^{3+} and B^{5+} centers has a negligible effect on the optical properties of these materials.⁴⁰ However, ordered vs. disordered B -site cation configurations alter the concentration-dependence of the electrical conductivity (σ). The conductivity is directly proportional to the antimony concentration in the disordered $\text{Cs}_2\text{Sb}_{1-x}\text{In}_x\text{Cl}_6$ series ($\sigma \propto [\text{Sb}]$), in contrast to the ordered $\text{Cs}_2\text{Sb}_{1-x}\text{Sn}_x\text{Cl}_6$ series, in which the conductivity is proportional to the concentration squared ($\sigma \propto [\text{Sb}]^2$).⁴¹ The crystal-chemical origins of these differences merit further investigation.

Lattice Dynamics and Electron-Phonon Coupling

Early research efforts of vacancy-ordered double perovskites were devoted to understanding the structural and dynamic behavior of these molecular-like crystals. Vacancy-ordered double perovskites exhibit cooperative octahedral tilting motifs familiar to ordered double perovskites,^{42,43} which are nominally driven by a size mismatch between the *A*-site cations and the surrounding $[BX_6]$ octahedral framework. The tendency of a given composition to exhibit octahedral tilting at room temperature can be predicted by the geometric “radius ratio,” which is defined as the ratio of the *A*-site cation ionic radius to the radius of the enclosing void formed by twelve *X*-site anions.^{11,44} The radius ratio (*R*) is calculated as $R = r_A / (D_{xx} - r_X)$, where r_A is the radius of the *A*-site cation, D_{xx} is the interoctahedral *X*–*X* bond length, and r_X is the radius of the *X*-site anion. When $0.89 < R < 1$, no octahedral tilting is expected at room temperature. Smaller *A*-site cations yield $R < 0.89$, and the octahedral framework will undergo cooperative tilting to optimize coordination to the *A*-site cation.⁴⁵ This is exemplified by the $A_2\text{TeI}_6$ (*A* = Cs^+ , Rb^+ , K^+) family; while Cs_2TeI_6 adopts the cubic vacancy-ordered double perovskite structure (space group $Fm\bar{3}m$),⁴⁶ replacing the larger Cs^+ cation with the smaller Rb^+ and K^+ cations yields cooperative octahedral tilting to lower symmetry structures ($P4/mnc$ and $P2_1/n$, respectively), as illustrated in Figure 8.^{47,48}

Figure 8: Crystal structures of Cs_2TeI_6 , Rb_2TeI_6 , and K_2TeI_6 as representative examples of common octahedral tilting motifs observed in the vacancy-ordered double perovskite family.

Octahedral rotations are a well-known origin of lattice dynamics in vacancy-ordered double

perovskites, and they are dictated by the size and bonding preferences of the A-site cation. In the $A_2\text{PtCl}_6$ series ($A = \text{K}^+$, Rb^+ , and Cs^+), the frequency of the rotary phonon mode increases with increasing size of the alkali cation.⁴⁹ Softening of these dynamic rotations upon cooling are also responsible for symmetry lowering phase transitions characterized by frozen-in cooperative octahedral tilts.^{49–57} In Rb_2SnI_6 , lower symmetry structures are observed due to the smaller size of the Rb^+ ion, which is significantly underbonded in the previously reported cubic vacancy-ordered double perovskite structure;^{18,58} the bond valence of the Rb^+ ion is significantly improved by cooperative octahedral tilting to the lower-symmetry tetragonal and monoclinic structural variants of the vacancy-ordered double perovskite structure. In the absence of cooperative octahedral tilting, anharmonic lattice dynamics may be observed when the coordination preferences of the A-site cation are dissatisfied by the cuboctahedral void. For example, both Cs_2SnI_6 and Cs_2TeI_6 crystallize in the cubic vacancy-ordered double perovskite structure, and neither compound undergoes phase transitions upon cooling, indicating that both compounds are dynamically stable.¹³ However, the local coordination environment reveals signatures of anharmonicity across the solid solution $\text{Cs}_2\text{Sn}_{1-x}\text{Te}_x\text{I}_6$, attributed to octahedral rotations coupled with off-centering of the Cs^+ ion. The degree of anharmonicity is correlated with the bond valence of the Cs^+ ion, such that the anharmonicity is minimized when the Cs^+ is optimally coordinated by the surrounding octahedral framework.⁵⁹

Dynamic organic cations (*e.g.*, plastic crystals) further contribute to the structural and dynamic behavior of vacancy-ordered double perovskites through complex interactions with the surrounding octahedra, with hydrogen bonding playing a significant role. In the $A_2\text{PtI}_6$ series with varied organic A-site cations, $(\text{NH}_4)_2\text{PtI}_6$ adopts the cubic vacancy-ordered double perovskite structure while $(\text{CH}_3\text{NH}_3)_2\text{PtI}_6$ yields a rhombohedral structural variant (space group $R\bar{3}m$). Incorporation of the larger $\text{CH}(\text{NH}_2)_2^+$ results in the monoclinic structural variant of the vacancy-ordered double perovskite structure (low-T K_2SnCl_6 , space group $P2_1/n$), while $(\text{C}(\text{NH}_2)_3)_2\text{PtI}_6$ adopts the hexagonal, non-perovskite K_2MnF_6 structure. By ^1H NMR relaxation experiments, Evans *et al.* demonstrated that the smaller NH_4^+ and CH_3NH_3^+ cations undergo rapid molecular reorienta-

tions, but the larger $\text{CH}(\text{NH}_2)_2^+$ and $\text{C}(\text{NH}_2)_3^+$ cations were observed to reorient over much slower timescales. Examination of the DFT-relaxed structures of $(\text{CH}(\text{NH}_2)_2)_2\text{PtI}_6$ and $(\text{C}(\text{NH}_2)_3)_2\text{PtI}_6$ indicates orientations of the organic cations that yield $\text{N}-\text{H}\cdots\text{I}$ distances that are characteristic of hydrogen bonds, suggesting an origin for the unique structural topologies and sluggish molecular dynamics in these compounds. Hydrogen bonding interactions may further drive anharmonic behavior through organic-inorganic coupling. In the hybrid vacancy-ordered double perovskites $(\text{CH}_3\text{NH}_3)_2\text{SnI}_6$ and $(\text{CH}(\text{NH}_2)_2)_2\text{SnI}_6$, coupling between the organic cations and the iodide sublattice yields soft, anharmonic lattice dynamics that manifest in the local coordination environment relative to Cs_2SnI_6 , despite the observation that all three compounds crystallize in the same cubic vacancy-ordered double perovskite structure by X-ray diffraction.¹⁷

It is further interesting to note the room-temperature structural differences between $(\text{CH}_3\text{NH}_3)_2\text{SnI}_6$ and $(\text{CH}(\text{NH}_2)_2)_2\text{SnI}_6$ and their Pt-I analogs. While the Sn-based compounds appear to adopt the cubic vacancy-ordered double perovskite structure at room temperature,¹⁷ other structural topologies characterized by rotations and tilting of the isolated $[\text{BX}_6]$ octahedra are observed in the Pt analogs.²⁵ As Sn^{4+} and Pt^{4+} exhibit similar ionic radii ($r_{\text{Sn}} = 0.690 \text{ \AA}$, $r_{\text{Pt}} = 0.625 \text{ \AA}$),⁶⁰ it is important to consider the effect of Sn-I vs. Pt-I covalency and/or electronegativity and the subsequent influence upon interoctahedral I-I van der Waals interactions and $\text{N}-\text{H}\cdots\text{I}$ hydrogen bonds in these compounds. The absence of extended polyhedral connectivity in vacancy-ordered double perovskites alleviates the competition between cooperative octahedral tilting and hydrogen bonding interactions often observed in ABX_3 perovskites,⁶¹ and therefore the phase transitions in hybrid vacancy-ordered double perovskites are predominantly driven by organic-inorganic coupling through non-covalent interactions, such as hydrogen bonding.

Lattice dynamics participate in the charge transport processes of perovskite halide semiconductors through electron-phonon coupling within the soft and deformable lattice. The formation of a polaron, in which an electron forms a localized deformation of the lattice, is a prevailing hypothesis to explain the long carrier excited state lifetimes yet only moderate carrier mobilities observed in perovskite halides such as methylammonium lead iodide.⁶² In conventional perovskite

halides, polarons form predominantly within the metal halide octahedral framework via $X-B-X$ bending and $B-X$ stretching modes, resulting in deformations and cooperative tilting of the $[BX_6]$ octahedra.^{63–66} It therefore follows that similar electron-phonon coupling processes occur in the vacancy-ordered double perovskites and may even be enhanced by the presence of relatively decoupled octahedral units.^{14,67}

As the lattice dynamics of vacancy-ordered double perovskites are intimately linked with the A-site cation species and its interaction with the surrounding octahedral framework, the electron-phonon coupling behavior in vacancy-ordered double perovskites follows trends predicted by the perovskite tolerance factor. As shown in Figure 9, the trend in experimental carrier mobilities across the $A_2\text{SnI}_6$ series is reproduced by computationally-derived carrier mobilities calculated within a polaron model, indicating that electron-phonon coupling processes dominate the charge transport behavior in vacancy-ordered double perovskites. These trends are also correlated with the perovskite tolerance factor. In Rb_2SnI_6 , the smaller size of the Rb^+ ion yields a tolerance factor less than 1 and produces a structure characterized by cooperative octahedral tilting.¹⁸ The lower symmetry structure further yields a larger number of non-degenerate low-frequency phonons that contribute to stronger electron-phonon coupling processes that account for experimental carrier mobilities that are ~ 50 -fold lower than those of the cubic Cs_2SnI_6 . On the other hand, introducing the larger organic CH_3NH_3^+ and $\text{CH}(\text{NH}_2)_2^+$ cations yields tolerance factors greater than 1 and reduced carrier mobilities relative to Cs_2SnI_6 . In these compounds, the larger interoctahedral I–I distances produces softer lattices which result in stronger electron-phonon interactions and subsequently reduced carrier mobilities.¹⁷ The highest carrier mobilities are observed for Cs_2SnI_6 with a tolerance factor of ~ 1 , suggesting that weaker electron-phonon coupling interactions are observed when the vacancy-ordered double perovskite lattice does not exhibit dynamic instabilities or anharmonicity. While polaron formation is expected to occur within the octahedral framework as in ABX_3 perovskite halides,^{63,66} the choice of A-site cation strongly influences the charge transport characteristics of vacancy-ordered double perovskites through coupling to the neighboring octahedra.

Figure 9: The experimental and calculated electron mobilities of the A_2SnI_6 vacancy-ordered double perovskites plotted as a function of perovskite tolerance factor. The experimentally-determined electron mobilities are shown as filled purple circles on the left axis, while the calculated Hellwarth electron mobilities are denoted by open orange squares on the right axis. Figure reproduced with permission from Maughan, Ganose, Almaker, Scanlon, Neilson, *Chem. Mater.*, **2018**, 30, 3909–3919.¹⁸

Concluding Remarks

Vacancy-ordered double perovskite semiconductors inhabit a rich compositional, structural, and dynamic phase space that may be accessed and tuned by compositional modification at all three sites to elicit desirable optical and electronic properties. Incorporating smaller X -site halogens is accompanied by a depression of the ionization potential and widening of the band gap due to halide p orbitals that dominate the valence band maximum. The close-packed lattice of large halides provides substantial orbital overlap between the neighboring isolated octahedra, yielding relatively low carrier effective masses and presumably higher carrier mobilities. Substitution of halogens with a smaller spatial distribution of the p orbitals results in reduced band dispersions and larger carrier effective masses. Compositional modification at the B -site at the center of the octahedra offers the greatest degree of flexibility to elicit desired properties and chemistries in vacancy-ordered double perovskites due to the large variety of tetravalent ions that may be accommodated into the structure. The B -site cations and their interaction with the halide ligands in the octahedra dictate energy and dispersion of the conduction band, the direct vs. indirect nature of the band gap, and the defect chemistry in vacancy-ordered double perovskites. The formally tetravalent

charge state of the *B*-site can also enable charge disproportionation and mixed valency, which gives rise to strong charge-transfer and unique vibronic coupling effects. The *A*-site cation does not directly participate in charge transport or optical absorption processes, but rather influences the surrounding octahedral framework through anharmonic lattice dynamics or cooperative octahedral tilting. Smaller *A*-site cations introduce cooperative octahedral tilting distortions that increase the magnitude of the band gap and carrier effective masses due to deviations in the close-packed halogen sublattice. Larger and more complex organic cations drive unique structural topologies and anharmonic lattice dynamics due to organic-inorganic coupling effects through hydrogen bonding. Changes to the dynamic landscape of vacancy-ordered double perovskites brought about by the choice of *A*-site cation further give rise to electron-phonon coupling interactions that strongly influence the charge transport behavior in these materials. These materials exhibit cooperative behavior (*e.g.*, charge transport, phase transitions) that reveals the importance of interoctahedral interactions. Due to the large range of accessible chemistries available at all three crystallographic sites, the vacancy-ordered double perovskite structure provides an ideal framework to determine structure-dynamics-property relationships in complex semiconductors for transformative advances in sustainable energy technologies.

Acknowledgments

References

- (1) Yang, W. S.; Park, B.-W.; Jung, E. H.; Jeon, N. J.; Kim, Y. C.; Lee, D. U.; Shin, S. S.; Seo, J.; Kim, E. K.; Noh, J. H.; Seok, S. I. Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells. *Science* **2017**, *356*, 1376–1379.
- (2) Hailegnaw, B.; Kirmayer, S.; Edri, E.; Hodes, G.; Cahen, D. Rain on methylammonium lead iodide based perovskites: possible environmental effects of perovskite solar cells. *J. Phys. Chem. Lett.* **2015**, *6*, 1543–1547.

- (3) Nagabhushana, G.; Shivaramaiah, R.; Navrotsky, A. Direct calorimetric verification of thermodynamic instability of lead halide hybrid perovskites. *Proc. Natl. Acad. Sci. U.S.A.* **2016**, *113*, 7717–7721.
- (4) Stoumpos, C. C.; Cao, D. H.; Clark, D. J.; Young, J.; Rondinelli, J. M.; Jang, J. I.; Hupp, J. T.; Kanatzidis, M. G. Ruddlesden–Popper hybrid lead iodide perovskite 2D homologous semiconductors. *Chem. Mater.* **2016**, *28*, 2852–2867.
- (5) Slavney, A. H.; Hu, T.; Lindenberg, A. M.; Karunadasa, H. I. A bismuth-halide double perovskite with long carrier recombination lifetime for photovoltaic applications. *J. Am. Chem. Soc.* **2016**, *138*, 2138–2141.
- (6) McClure, E. T.; Ball, M. R.; Windl, W.; Woodward, P. M. Cs₂AgBiX₆ (X = Br, Cl): New Visible Light Absorbing, Lead-Free Halide Perovskite Semiconductors. *Chem. Mater.* **2016**, *28*, 1348–1354.
- (7) Lee, B.; Stoumpos, C. C.; Zhou, N.; Hao, F.; Malliakas, C.; Yeh, C.-Y.; Marks, T. J.; Kanatzidis, M. G.; Chang, R. P. Air-stable molecular semiconducting iodosalts for solar cell applications: Cs₂SnI₆ as a hole conductor. *J. Am. Chem. Soc.* **2014**, *136*, 15379–15385.
- (8) Xiao, Z.; Zhou, Y.; Hosono, H.; Kamiya, T. Intrinsic Defects in a Photovoltaic Perovskite Variant Cs₂SnI₆. *Phys. Chem. Chem. Phys.* **2015**, *17*, 18900–18903.
- (9) Chung, I.; Song, J.-H.; Im, J.; Androulakis, J.; Malliakas, C. D.; Li, H.; Freeman, A. J.; Kenney, J. T.; Kanatzidis, M. G. CsSnI₃: Semiconductor or Metal? High Electrical Conductivity and Strong Near-Infrared Photoluminescence from a Single Material. High Hole Mobility and Phase-Transitions. *J. Am. Chem. Soc.* **2012**, *134*, 8579–8587.
- (10) Xiao, Z.; Hosono, H.; Kamiya, T. Origin of Carrier Generation in Photovoltaic Perovskite Variant Cs₂SnI₆. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1250–1255.

- (11) Cai, Y.; Xie, W.; Ding, H.; Chen, Y.; Thirumal, K.; Wong, L. H.; Mathews, N.; Mhaisalkar, S. G.; Sherburne, M.; Asta, M. Computational Study of Halide Perovskite-Derived A_2BX_6 Inorganic Compounds: Chemical Trends in Electronic Structure and Structural Stability. *Chem. Mater.* **2017**, *29*, 7740–7749.
- (12) Kaltzoglou, A.; Antoniadou, M.; Kontos, A. G.; Stoumpos, C. C.; Perganti, D.; Siranidi, E.; Raptis, V.; Trohidou, K.; Psycharis, V.; Kanatzidis, M. G.; Falaras, P. Optical-vibrational properties of the Cs_2SnX_6 ($X = Cl, Br, I$) defect perovskites and hole-transport efficiency in dye-sensitized solar cells. *J. Phys. Chem. C* **2016**, *120*, 11777–11785.
- (13) Maughan, A. E.; Ganose, A. M.; Bordelon, M. M.; Miller, E. M.; Scanlon, D. O.; Neilson, J. R. Defect tolerance to intolerance in the vacancy-ordered double perovskite semiconductors Cs_2SnI_6 and Cs_2TeI_6 . *J. Am. Chem. Soc.* **2016**, *138*, 8453–8464.
- (14) Huang, H.-M.; Jiang, Z.-Y.; Luo, S.-J. First-principles investigations on the mechanical, thermal, electronic, and optical properties of the defect perovskites Cs_2SnX_6 ($X = Cl, Br, I$). *Chin. Phys. B* **2017**, *26*, 096301.
- (15) Lee, B.; Krenselewski, A.; Baik, S. I.; Seidman, D. N.; Chang, R. P. Solution processing of air-stable molecular semiconducting iodosalts, $Cs_2SnI_{6-x}Br_x$, for potential solar cell applications. *Sustainable Energy Fuels* **2017**, *1*, 710–724.
- (16) Ju, M.-G.; Chen, M.; Zhou, Y.; Garces, H. F.; Dai, J.; Ma, L.; Padture, N. P.; Zeng, X. C. Earth-abundant nontoxic titanium (IV)-based vacancy-ordered double perovskite halides with tunable 1.0 to 1.8 eV bandgaps for photovoltaic applications. *ACS Energy Lett.* **2018**, *3*, 297–304.
- (17) Maughan, A. E.; Ganose, A. M.; Candia, A. M.; Granger, J. T.; Scanlon, D. O.; Neilson, J. R. Anharmonicity and Octahedral Tilting in Hybrid Vacancy-Ordered Double Perovskites. *Chem. Mater.* **2018**, *30*, 472–483.

- (18) Maughan, A. E.; Ganose, A. M.; Almaker, M. A.; Scanlon, D. O.; Neilson, J. R. Tolerance Factor and Cooperative Tilting Effects in Vacancy-Ordered Double Perovskite Halides. *Chem. Mater.* **2018**, *30*, 3909–3919.
- (19) Dalpian, G. M.; Liu, Q.; Stoumpos, C. C.; Douvalis, A. P.; Balasubramanian, M.; Kanatzidis, M. G.; Zunger, A. Changes in charge density vs changes in formal oxidation states: The case of Sn halide perovskites and their ordered vacancy analogues. *Phys. Rev. Mater.* **2017**, *1*, 025401.
- (20) Huang, L.-y.; Lambrecht, W. R. Electronic band structure, phonons, and exciton binding energies of halide perovskites CsSnCl₃, CsSnBr₃, and CsSnI₃. *Phys. Rev. B* **2013**, *88*, 165203.
- (21) Zhang, J.; Yu, C.; Wang, L.; Li, Y.; Ren, Y.; Shum, K. Energy barrier at the N719-dye/CsSnI₃ interface for photogenerated holes in dye-sensitized solar cells. *Sci. Rep.* **2014**, *4*, 6954–6959.
- (22) Saparov, B.; Sun, J.-P.; Meng, W.; Xiao, Z.; Duan, H.-S.; Gunawan, O.; Shin, D.; Hill, I. G.; Yan, Y.; Mitzi, D. B. Thin-film deposition and characterization of a Sn-deficient perovskite derivative Cs₂SnI₆. *Chem. Mater.* **2016**, *28*, 2315–2322.
- (23) Funabiki, F.; Toda, Y.; Hosono, H. Optical and Electrical Properties of Perovskite Variant (CH₃NH₃)₂SnI₆. *J. Phys. Chem. C* **2018**, *122*, 10749–10754.
- (24) Sakai, N.; Haghighirad, A. A.; Filip, M. R.; Nayak, P. K.; Nayak, S.; Ramadan, A.; Wang, Z.; Giustino, F.; Snaith, H. J. Solution-processed cesium hexabromopalladate (IV), Cs₂PdBr₆, for optoelectronic applications. *J. Am. Chem. Soc.* **2017**, *139*, 6030–6033.
- (25) Evans, H. A.; Fabini, D. H.; Andrews, J. L.; Koerner, M.; Preefer, M. B.; Wu, G.; Wudl, F.; Cheetham, A. K.; Seshadri, R. Hydrogen Bonding Controls the Structural Evolution in Perovskite-Related Hybrid Platinum (IV) Iodides. *Inorg. Chem.* **2018**,
- (26) Ganose, A. M. Atomic-scale insights into emergent photovoltaic absorbers. Ph.D. thesis, University College London, 2018.

- (27) Kaltzoglou, A.; Antoniadou, M.; Perganti, D.; Siranidi, E.; Raptis, V.; Trohidou, K.; Psycharis, V.; Kontos, A. G.; Falaras, P. Mixed-halide $\text{Cs}_2\text{SnI}_3\text{Br}_3$ perovskite as low resistance hole-transporting material in dye-sensitized solar cells. *Electrochim. Acta* **2015**, *184*, 466–474.
- (28) Chen, M.; Ju, M.-G.; Carl, A. D.; Zong, Y.; Grimm, R. L.; Gu, J.; Zeng, X. C.; Zhou, Y.; Padture, N. P. Cesium titanium (IV) bromide thin films based stable lead-free perovskite solar cells. *Joule* **2018**, *2*, 558–570.
- (29) Xiao, Z.; Meng, W.; Wang, J.; Mitzi, D. B.; Yan, Y. Searching for promising new perovskite-based photovoltaic absorbers: the importance of electronic dimensionality. *Mater. Horiz.* **2017**, *4*, 206–216.
- (30) Zakutayev, A.; Caskey, C. M.; Fioretti, A. N.; Ginley, D. S.; Vidal, J.; Stevanovic, V.; Tea, E.; Lany, S. Defect tolerant semiconductors for solar energy conversion. *J. Phys. Chem. Lett.* **2014**, *5*, 1117–1125.
- (31) Prassides, K.; Day, P.; Cheetham, A. K. Anion ordering in mixed valence dicesium hexachloroantimonate (Cs_2SbCl_6) and related salts. *J. Am. Chem. Soc.* **1983**, *105*, 3366–3368.
- (32) Robin, M. B.; Day, P. *Molecules Into Materials: Case Studies in Materials Chemistry—Mixed Valency, Magnetism and Superconductivity*; World Scientific, 2007; pp 142–317.
- (33) Lawton, S. L.; Jacobson, R. A. Crystal Structure Studies of Some Unusual Antimony Bromide Salts. *J. Am. Chem. Soc.* **1966**, *88*, 616–618.
- (34) Lawton, S. L.; Jacobson, R. A. The Crystal Structure of Ammonium Hexabromoantimonate, $(\text{NH}_4)_4\text{Sb}^{\text{III}}\text{Sb}^{\text{V}}\text{Br}_{12}$. *Inorg. Chem.* **1966**, *5*, 743–749.
- (35) Prassides, K.; Day, P.; Cheetham, A. K. Crystal structures of mixed-valency and mixed-metal salts $\text{A}_2\text{M}^{\text{III}}_{0.5}\text{Sb}^{\text{V}}_{0.5}\text{X}_6$ (A = Rb, Cs; M = Sb, Bi, In, Tl, Fe, Rh; X = Cl, Br). A powder neutron diffraction study. *Inorg. Chem.* **1985**, *24*, 545–552.

- (36) Day, P. Spectra and constitution of antimony (III), antimony (V) hexahalide salts and related compounds. *Inorg. Chem.* **1963**, 2, 452–456.
- (37) Clark, R. J.; Trumble, W. R. Resonance Raman spectra of some mixed-valence halogeno-compounds of antimony and lead. *J. Chem. Soc. Dalton Trans.* **1976**, 1145–1149.
- (38) Clark, H.; Swanson, B. I. Effects of outer-sphere electron transfer on the vibrational spectrum of dicesium antimony hexachloride. *J. Am. Chem. Soc.* **1981**, 103, 2928–2933.
- (39) Prassides, K.; Day, P. Phonons in mixed-valency and mixed-metal salts $A_2M_{0.5}Sb_{0.5}Cl_6$ (A = Rb, Cs; M = Sb, Bi, Tl): an inelastic neutron scattering study. *Inorg. Chem.* **1985**, 24, 3035–3043.
- (40) Atkinson, L.; Day, P. Charge transfer in mixed-valence solids. Part IV. Electronic spectra of hexachloroantimonates (III, V). *J. Chem. Soc. A* **1969**, 2423–2431.
- (41) Atkinson, L.; Day, P. Charge transfer in mixed-valence solids. Part V. Semiconductivity of hexachloroantimonates (III, V). *J. Chem. Soc. A* **1969**, 2432–2436.
- (42) Woodward, P. M. Octahedral tilting in perovskites. I. Geometrical considerations. *Acta Crystallogr. B* **1997**, 53, 32–43.
- (43) Howard, C. J.; Kennedy, B. J.; Woodward, P. M. Ordered double perovskites – a group-theoretical analysis. *Acta Crystallogr. B* **2003**, 59, 463–471.
- (44) Brown, I. D. The crystal structure of K_2TeBr_6 . *Can. J. Chem.* **1964**, 42, 2758–2767.
- (45) Young, J.; Rondinelli, J. M. Octahedral Rotation Preferences in Perovskite Iodides and Bromides. *J. Phys. Chem. Lett.* **2016**, 7, 918–922.
- (46) Sidey, V.; Zubaka, O.; Stercho, I.; Peresh, E. Y. X-ray Rietveld structure refinement and bond-valence analysis of Cs_2TeI_6 . *Chem. Met. Alloys* **2010**, 108–114.

- (47) Abriel, W. Crystal structure and phase transition of Rb_2TeI_6 . *Mat. Res. Bull.* **1982**, *17*, 1341–1346.
- (48) Syoyama, S.; Osaki, K.; Kusanagi, S. X-ray Study of the Crystal Structure of K_2TeI_6 and the Symmetry of the Compounds of This Series. *Inorg. Nucl. Chem. Letters* **1972**, *8*, 181–184.
- (49) Armstrong, R. L.; Jeffrey, K. R. Quadrupolar Nuclear Spin–Lattice Relaxation in R_2MX_6 Compounds. *Can. J. Phys.* **1971**, *49*, 49–53.
- (50) O’Leary, G.; Wheeler, R. Phase transitions and soft librational modes in cubic crystals. *Phys. Rev. B* **1970**, *1*, 4409.
- (51) Cooke, D. F.; Armstrong, R. L. Investigation of the Rotary Lattice Mode in R_2PtCl_6 Compounds. I. From Measurements of the ^{35}Cl Nuclear Quadrupole Resonance Frequency. *Can. J. Phys.* **1971**, *49*, 2381–2388.
- (52) Armstrong, R. L.; Cooke, D. F. Investigation of the Rotary Lattice Mode in R_2PtCl_6 Compounds. II. From a Study of the ^{35}Cl Nuclear Quadrupolar Spin–Lattice Relaxation. *Can. J. Phys.* **1971**, *49*, 2389–2395.
- (53) van Driel, H. M.; Armstrong, R. L.; McEnnan, M. M. Soft-mode behavior near the 111-K displacive phase transition in K_2ReCl_6 . *Phys. Rev. B* **1975**, *12*, 488.
- (54) Lynn, J.; Patterson, H.; Shirane, G.; Wheeler, R. Soft rotary mode and structural phase transitions in K_2ReCl_6 . *Solid State Commun.* **1978**, *27*, 859–862.
- (55) McElroy, R. G.; Armstrong, R. L. Cubic to tetragonal phase transitions in $(\text{NH}_4)_2\text{PtBr}_6$ and Rb_2PtI_6 . *Phys. Rev. B* **1978**, *18*, 1352.
- (56) Patterson, H.; Lynn, J. Lattice-dynamics study of Cs_2SiF_6 with application to the vibronic optical spectra of MnF_6^{-2} in Cs_2SiF_6 . *Phys. Rev. B* **1979**, *19*, 1213.
- (57) Waschke, V.; Pelzl, J.; Höck, K.-H.; Eckold, G. Inelastic neutron scattering from transverse acoustic modes in K_2SnCl_6 . *Solid State Commun.* **1984**, *52*, 829–831.

- (58) Werker, W. Die Krystallstruktur des Rb_2SnI_6 und Cs_2SnI_6 . *Recl. Trav. Chim. Pays-Bas* **1939**, 58, 257–258.
- (59) Maughan, A. E.; Paecklar, A. A.; Neilson, J. R. Bond valences and anharmonicity in vacancy-ordered double perovskite halides. *J. Mater. Chem. C* **2018**, DOI: 10.1039/c8tc03527j.
- (60) Shannon, R.; Prewitt, C. Revised values of effective ionic radii. *Acta Crystallogr. B* **1970**, 26, 1046–1048.
- (61) Mozur, E. M.; Maughan, A. E.; Cheng, Y.; Huq, A.; Jalarvo, N.; Daemen, L. L.; Neilson, J. R. Orientational Glass Formation in Substituted Hybrid Perovskites. *Chem. Mater.* **2017**, 29, 10168–10177.
- (62) Zhu, X.-Y.; Podzorov, V. Charge carriers in hybrid organic–inorganic lead halide perovskites might be protected as large polarons. *J. Phys. Chem. Lett.* **2015**, 6, 4758–4761.
- (63) Miyata, K.; Meggiolaro, D.; Trinh, M. T.; Joshi, P. P.; Mosconi, E.; Jones, S. C.; De Angelis, F.; Zhu, X.-Y. Large polarons in lead halide perovskites. *Sci. Adv.* **2017**, 3, e1701217.
- (64) Wu, X. et al. Light-induced picosecond rotational disordering of the inorganic sublattice in hybrid perovskites. *Sci. Adv.* **2017**, 3, e1602388.
- (65) Guzelturk, B.; Belisle, R. A.; Smith, M. D.; Bruening, K.; Prasanna, R.; Yuan, Y.; Gopalan, V.; Tassone, C. J.; Karunadasa, H. I.; McGehee, M. D.; Lindenberg, A. M. Terahertz Emission from Hybrid Perovskites Driven by Ultrafast Charge Separation and Strong Electron–Phonon Coupling. *Adv. Mater.* **2018**, 30, 1704737.
- (66) Park, M.; Neukirch, A. J.; Tretiak, S.; Park, M.; Reyes-Lillo, S. E.; Lai, M.; Ellis, S. R.; Dietze, D.; Neaton, J. B.; Yang, P.; Mathies, R. A. Excited-State Vibrational Dynamics Toward the Polaron in Methylammonium Lead Iodide (MAPbI_3) Perovskite. *Nat. Commun.* **2018**, 9, 1–8.

- (67) Yuan, G.; Huang, S.; Niu, J.; Qin, S.; Wu, X.; Ding, H.; Lu, A. Compressibility of Cs_2SnBr_6 by X-ray diffraction and Raman spectroscopy. *Solid State Commun.* **2018**, 275, 68–72.