Double Perovskites

Doubling the Stakes: The Promise of Halide Double Perovskites

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Dedicated to Prof. Harry B. Gray on the occasion of his 85th birthday
When the stakes are doubled in a wager, a player must correctly place two consecutive bets to win, but the payout is larger. Similarly, two B sites in combination dictate the properties of $A_xB_yX_z$ (A = monocation, X = halide) double perovskites. Correctly picking two B sites is more challenging than picking just one, as in the $A^+BX_3$ single perovskites, but the options are greater and, we believe, the rewards are higher when the stakes are doubled. In this Minireview, we emphasize fundamental aspects of halide double perovskites to provide a foundation for interested readers to explore this extraordinary class of materials. In particular, we highlight the differences and similarities between double and single perovskites and describe how the double perovskite structure potentially offers greater control over photophysical properties.

1. Introduction

Halide perovskites, which date back to the 1800s,[1] are crystalline semiconductors formed in solution-state or mild solid-state reactions. These ionic solids consist of anionic metal-halide octahedra connected in 0, 1, 2, or 3 dimensions through shared corners, with inorganic or organic cations providing charge compensation. Research efforts on three-dimensional (3D) lead-halide perovskites have recently been invigorated due to the remarkable rise in the efficiencies of solar cells employing these materials as absorbers, specifically, (MA)PbI$_3$ (MA = CH$_3$NH$_3$)$^+$ and its derivatives.[3] However, lead perovskites constitute only a small section of the vast and diverse family of halide perovskites. Thus, more recently, researchers have sought to cast a wider net in search of new compositions that mimic the optoelectronic properties of the lead perovskites.[5] These efforts seek to both understand the origin of the remarkable optoelectronic properties of lead perovskites through fundamental studies and to identify functional analogues with improved stability as well as reduced toxicity and environmental impact.[6] Of all the alternatives that have been explored, the A$_2$BBX$_6$ (A = monocation, X = halide) double perovskites have emerged as the most abundant and promising family.[6a] Double perovskites maintain a similar structural framework to that found in single perovskites while permitting a wider variety of cations to be incorporated into the octahedrally coordinated B/B site. This enables access to an expansive range of alternative compositions and electronic structures, which researchers are only beginning to explore.

Herein, we discuss select structural and optoelectronic topics relevant to contemporary research on halide double perovskites. This Minireview will not address nanostructuring[6b] or detail device applications,[7] except for a brief discussion of the latter in the concluding section. In Section 1, we define double perovskites and briefly survey their history. Section 2 discusses different subclasses of double perovskites, including their two-dimensional (2D) variants and the local structural distortions that occur in these materials. Section 3 gives an overview of double perovskite electronic structures and highlights simple rules that predict the electronic structures of undiscovered compounds. In Section 4, we detail strategies for modifying the electronic structure. We conclude in Section 5 by emphasizing commonalities between double perovskites and other well-known materials families, which we hope will provide direction for future studies.

1.1. Definition of 3D Double Perovskites

As a materials family with a long, rich history, double perovskites have acquired various definitions, which are the subject of continuing discussion.[8] For the purposes of this Minireview, we follow a relatively restrictive definition of 3D halide double perovskites by including only materials that meet the following criteria:

1. The structure contains cations or vacancies surrounded by six halides ([BX$_6$]$^{n-}$: B = cation or vacancy; X = halide).
2. The [BX$_6$]$^{n-}$ units are exclusively corner-sharing in a 3D pattern (B = cation or vacancy; X = halide).
3. There are exactly two structurally distinguishable [BX$_6$]$^{n-}$ motifs in the unit cell, such that the chemical formula must be $A_xBB'X_n$ (B = cation or vacancy; X = halide).

The third criterion, requiring exactly two distinct [BX$_6$]$^{n-}$ units, distinguishes double perovskites from single perovskites (Figure 1). The ordering of these distinct [BX$_6$]$^{n-}$ units significantly impacts the material’s electronic structure (see Section 3).[9] Fully disordered alloys with only one distinct B site, such as A(Ph$_3$Sn)$_x$X$_3$ (which were investigated as early as the 1970s[10] and recently used in solar cells[11]) are thus classified as single perovskites. In the oxide literature, materials with two distinct, ordered A sites (A(A’B)X$_3$) are commonly considered double perovskites.[12] We exclude such compositions from our definition because examples of A-site ordered halide perovskites are extremely rare[13] and because such materials are expected to exhibit optoelectronic properties more similar to those of single perovskites (see Section 3.1).

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1.2. Double Perovskite Nomenclature

Although the term “double perovskite” conveniently includes all halide perovskites with distinct B and B’ sites, historically the $A_2BIBIIIX_6$ and the $A_2BIVX_6$ ($\Box = \text{vacancy}$) perovskites have been considered as separate families. In the older literature, the $A_2BIBIIIX_6$ compounds are known as elpasolites after the mineral elpasolite, $K_2NaAlF_6$.\cite{1a,14} The $A_2BIVX_6$ perovskites have been known by many names over the decades, including double halides,\cite{15} complex antifluorites,\cite{16} hexahalogenometallates,\cite{17} and, most recently, vacancy-ordered double perovskites.\cite{18} Here, we refer to these materials as “$K_2PtCl_6$-type perovskites” after one of the early $A_2BIVX_6$ compounds to be structurally characterized.\cite{19} In the following sections, we give a brief overview of the historical development of these two subdivisions of double perovskites, highlighting important bodies of work and key milestones in Figure 2.

1.3. History of Elpasolites

Elspasolites have been known since the late 19th century\cite{1a,14} and predate the development of X-ray diffraction. The earliest report appears to be the 1883 discovery of the mineral elpasolite, $K_2NaAlF_6$, identified by the distinctive 2:1:1:6 ratio in the elemental analysis of rock samples near Pikes Peak in El Paso County, Colorado, USA.\cite{1a} The first reported synthesis of an elpasolite was of $Cs_2AuIAuIIICl_6$ in 1922.\cite{20} The early application of X-ray crystallography revealed the atomic structure of $K_2NaAlF_6$ in 1932,\cite{21} although the space group was incorrectly assigned,\cite{22} and the structures of $Cs_2AuIAuIIICl_6$ and $Cs_2AgIAuIIICl_6$ in 1938 (Figure 1).\cite{23} Until the 1970s, additional studies on elpasolites were largely

Figure 1. A sample of known double perovskite structures demonstrating the structural and compositional diversity of this family. From the top proceeding clockwise, the crystal structures of: $K_2NaAlF_6$, $K_2PtCl_6$, $(MA)_2TlBiBr_6$ (MA = methylammonium), $(FA)_2SnI_6$ (FA = formamidinium), and $Cs_2Au/AgIIICl_6$. The single perovskite $(MA)PbI_3$ is shown in the middle. Atom colors: dark green = Na, light blue = Al, dark orange = Pt, light-orange = Bi, dark red = Sn, dark blue = AuIII, light pink = AuI, turquoise = Pb, magenta = K, teal = Cs, purple = I, brown = Br, green = Cl, yellow = F, gray = C, and blue = N; H atoms are omitted.

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structural,[24] greatly increasing the number of known materials, particularly those containing lanthanides (Figure 3).[25] One vein of work, beginning in the 1970s, exploited the local octahedral site symmetry of elpasolites to study the magnetic and electronic properties of lanthanide-based structures[26] and to form luminescent materials through lanthanide or transition-metal doping.[27] Meanwhile, a separate body of work spanning more than 50 years explored mixed valency in elpasolites. Beginning in the 1950s, elpasolites with the general formula \( \text{Cs}_2\text{BAuIIIX}_6 \) (\( \text{B} = \text{AgI}, \text{AuI}, \text{X} = \text{Cl}, \text{Br}, \text{I} \)) were investigated as part of the widespread interest in mixed valency at the time.[28] These early studies laid the groundwork for experiments throughout the 1970s and 1980s, which probed how high pressure influences the structural and mixed-valence electronic properties of these materials.[29] In the 1990s, \( \text{Cs}_2\text{AuIAuIII}_6 \) gained renewed interest after the discovery of superconductivity in \((\text{Ba}_{1-x}\text{K}_x)^2\text{BiIIIBiVO}_6\), another mixed-valence double perovskite.[30] Although a semiconductor-to-metal transition was observed in \( \text{Cs}_2\text{AuIAuIII}_6 \) at high pressures,[31] attributed to the comproportionation of \( \text{AuI} \) and \( \text{AuIII} \) to \( \text{AuII} \),[32] no superconductivity has yet been observed. Nevertheless, the search for superconductivity in mixed-valence double perovskites continues, with more recent studies investigating \( \text{Cs}_2\text{TlITlIII}_6 \) (\( \text{X} = \text{F}, \text{Cl} \)).[33] The mixed-valence \( \text{AuII}\text{--AuIII} \) elpasolites returned to the scene in 2003 when Guloy and co-workers reported the first example of a 2D elpasolite \((\text{A})_2[(\text{AuII}_2)(\text{AuIII}_4)(\text{I}_3)]_2 \) (\( \text{A} = 1,8\text{-octanediiodonium or 1,7-heptanedioiodonium} \)),[34] where the 3D structure of \( \text{Cs}_2\text{AuIAuIII}_6 \) is thinned to a single sheet of corner-sharing octahedra (see Section 2.4), albeit with some terminal \( \text{I}^- \) ligands replaced by \( \text{I}_3^- \) ligands.[35]
1.4. History of K₂PtCl₆-Type Perovskites

The origin of K₂PtCl₆-type perovskites dates back to the synthesis of A₄TeX₆ (A = K⁺, Na⁺, NH₄⁺, and X = Cl⁻, Br⁻, I⁻) in 1834.[36] Before the 1920s, studies focused on synthesis, elemental analysis, and crystal morphology.[15,37] Large ionic cations were commonly employed as A-site cations, thus demonstrating the close association of K₂PtCl₆-type perovskites with molecular salts.[37b,d,38] A series of X-ray crystallographic studies in the 1920s showed that these materials consist of isolated octahedra (Figure 1).[19,39] The authors spectroscopy.[45] Additionally, much like elpasolites, K₂PtCl₆-type perovskites are excellent host structures for octahedral complexes (particularly for B²⁻[65] but only at such low levels that it is better discussed as antifluorites. Many more K₂PtCl₆-type perovskites were subsequently characterized,[40] and at least 30 elements have been incorporated at the B site to date (Figure 3).[41] A number of these materials exhibit symmetry-lowering octahedral rotations as a result of over- or undersized A-site cations (see Section 2.5.2).[42] A structural analysis, similar to the Goldschmidt tolerance factor,[43] was first developed in 1964 by Brown, which enabled prediction of cubic K₂PtCl₆-type perovskites and rationalized their temperature-dependent phase-change behavior.[42,44] The rapid diversification of the K₂PtCl₆-type perovskites led to a growing interest in their fundamental properties. Throughout the 1960s, these materials were used to investigate the covalency of the metal-halide bond of [BX₆]²⁻ octahedral complexes (particularly for B = third-row transition metal) using pure quadrupole resonance spectroscopy.[45] Additionally, much like elpasolites, K₂PtCl₆-type perovskites were found to be excellent host structures for metal alloying, facilitating the discovery of covalent π-bonding in IrCl₆²⁻ by electron paramagnetic resonance spectroscopy.[46] Charge transfer between mixed-valence Sb³⁺ and Sb⁵⁺ ions by optical spectroscopy,[47] and photon upconversion from Re⁴⁺ ions doped into a Cs₂ZrCl₆ host structure.[27d,48]

1.5. Recent Work

The recent revival of interest in halide double perovskites originates from the search for nontoxic alternatives to APbX₃ in perovskite photovoltaics.[4a] The first comments on the K₂PtCl₆-type perovskites in recent perovskite literature arose from the known[49] undesired oxidation of AsSnIH₃ to ASnIP₃, followed by a 2014 investigation of Cs₂SnI₆ for photovoltaic applications.[50] The following year, a computational paper proposed the hypothetical elpasolite (MA)₂TlBIX₉ as a potential photovoltaic absorber.[51] This early work did not refer to the subject materials as double perovskites. Recognition of the potential of the halide double perovskite family as a whole arrived in 2016, when three groups independently reported the synthesis and optoelectronic properties of the elpasolites Cs₂AgBiX₆ (X = Cl⁻ and/or Br⁻).[52] Since then, many new elpasolites have been synthesized, including Cs₂AgInCl₆,[53] Cs₂AgTIX₆ (X = Cl⁻, Br⁻)[54] Cs₂AgSbCl₆,[55] (MA)₂TlBIX₉ and various alloys.[56-58] This recent growth of novel elpasolite compositions has sparked an interest in many K₂PtCl₆-type perovskites well-known in the early literature, such as Cs₂TeI₆,[15] Cs₂PdBr₆,[59] Cs₂SnI₆,[58] Cs₂PtI₄,[40] and Cs₂TlI₂,[60] as researchers reinvestigate these materials in the context of photovoltaics.[18,61] The recent interest in halide double perovskites as photovoltaic absorbers has led to new applications for these materials[7] while also serving as a platform for more fundamental studies, such as investigations into the consequences of dimensional reduction.[62] In particular, a recent flurry of reports has increased the phase space of 2D elpasolites, starting with Ag-Bi in 2018[62a] and then expanding to Ag-Tl[62b] Ag-In[62c] and Cu-Bi.[62d] The young, but rapidly growing, field of lower-dimensional double perovskites is likely to greatly expand the structural and functional diversity of the double perovskite family in the coming years, as witnessed previously for the halide single perovskites.[63]

2. A Structural Survey

In the following sections, we discuss some of the most important aspects of the double perovskite structure, including B-site ordering, dimensional reduction, and structural distortion.

2.1. Thermodynamics of B-Site Ordering

B-site ordering distinguishes double perovskites from single perovskites. In halide double perovskites, this ordering is thermodynamically favored. For example, the complete disordering of the Ag⁺ and Bi³⁺ cations in Cs₂AgBiBr₆ is calculated to occur only above 3000 K.[64] At room temperature, entropically driven B-site disordering is likely present but only at such low levels that it is better discussed as a propensity for the formation of anti-site defects.[65] Similar to the case of the oxide perovskites, B-site ordering is likely driven by electrostatics, as having adjacent 3 + or 4 + cations is unfavorable.[66,67] Indeed, isovalent B and Y cations most
commonly form disordered single perovskites (e.g., A(Sn1−xPb)xI3). One notable exception is Cs7Hg3Pd6Cl19, where octahedral distortions drive B-site ordering. Likewise, in alloying studies, the speciation of the impurity cation in the host double perovskite depends strongly on its charge, generally resulting in isovalent substitution (see Section 4.1).[7a,18,57a,b]

2.2. B-Site Ordering Motifs

All known halide double perovskites display rock-salt ordering. Here, each [BX₆]⁻ unit is surrounded by six [B'X₆]⁺ units and vice versa, thereby forming a 3D checkerboard pattern reminiscent of the ordering of Na⁺ and Cl⁻ ions in the NaCl rock-salt structure. Intriguingly, octahedral distortions stabilize several more exotic forms of B-site ordering in the oxide perovskites,[67] including layered[68] and columnar arrangements.[6a,b,67] Such orderings may also be possible in the halides, although, to date, all halide double perovskites with highly distorted [BX₆]⁻ units display rock-salt ordering.[23,66]

2.3. Stoichiometric Vacancies

The K₂PtCl₆-type perovskite structure is equivalent to the elpasolite structure where one of the B sites is a vacancy (Figure 4B,C). Alternatively, the K₂PtCl₆-type perovskite structure can be viewed according to the definition of (111) perovskites set forth by Mitzi.[69] This perovskite family is derived from the single perovskite structure by slicing along a series of evenly spaced (111) crystallographic planes, effectively generating planes of B-site vacancies (Figure 4D). The index q refers to the number of metal halide layers lying between planes of vacancies. Although halide perovskites with q = 1, 2, and 3 have been reported,[63a,69,70] those with q = 2 (Figure 4E) and 3 do not fit our definition of double perovskites (see Section 1.1) or dimensionally reduced double perovskites (see Section 2.4). Only the q = 1 structure, where half of the B sites are replaced by vacancies, qualifies as a double perovskite.

2.4. Dimensional Reduction

Despite the extensive history of halide double perovskites, their lower-dimensional derivatives remained completely unexplored until relatively recently.[34,62a] We define lower-dimensional halide double perovskites as materials whose inorganic framework can be derived through dimensional reduction[71] of a 3D double perovskite (which, according to our definition in Section 1.1, requires an ordered arrangement of two distinct [BX₆]⁻ units). Whereas a structurally diverse array of lower-dimensional halide single perovskites exists,[60] such variety has not yet been achieved for halide double perovskites. In the following sections, we highlight the known structure types of layered double perovskites and identify missing topologies to motivate continued exploration.

2.4.1. The (001) Perovskites

To date, all examples of dimensionally reduced double perovskites[34,62a-c,72] belong to the (001) elpasolite family, where the inorganic framework is derived from a slice taken along the (001) crystallographic plane of the ABX₃ structure (Figure 5A).[69] This 2D perovskite structure consists of flat sheets of corner-sharing, alternating [BX₆]⁻ and [B'X₆]⁺ octahedra. These sheets can consist of one or multiple layers of stacked octahedra (Figure 5A). Thicker slabs require a specific ratio of small and large A-site cations. The larger A' monocations partition the 3D structure into sheets, while the smaller A cations occupy cuboctahedral cavities within the sheets, thereby yielding the general formula A'ₙA₂₋ₙBₐB'ₐ₋ₙX₆₋₂n, where n is the number of octahedral layers forming the inorganic slabs. Unlike in the tin- and lead-based materials, where layered perovskites with 1 ≤ n ≤ 7 have been crystallographically characterized,[73] thus far, only n = 1 and 2 members of the (001) elpasolites are known.[34,62a-c] Note that we have restricted our list of 2D double perovskites to those with demonstrated crystallographic B-site ordering. Nevertheless, there are several reports of 2D double perovskites with disordered 1+ and 3+ B-site cations, although it is so far unclear whether this disorder arises solely from a lack of registry between adjacent

Figure 5. Dimensional reduction of the 3D double perovskite framework to yield 2D double perovskites with different topologies. All known examples of lower-dimensional halide double perovskites belong to the (001) family (A); inorganic slabs with bilayer (n = 2) and monolayer (n = 1) thicknesses have been prepared. Pictured here from left to right are the single-crystal X-ray structures of 3D Cs₂Ag(TlBr)₂[74] and its n = 2 and n = 1 derivatives,[80] black, white, brown, teal, blue, and gray spheres represent TI, Ag, Br, Cs, N, and C atoms, respectively. H and disordered atoms are omitted for clarity. In (B) and (C), representations of hypothetical (110) and (111) 2D double perovskites, respectively, are shown. To date, there are no known examples of such materials, although these structure-types are known for single perovskites.

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perovskite sheets or also from a random distribution of the B-site cations within the same sheet.[62,74]

2.4.2. The (110) and (111) Perovskites

Lower-dimensional perovskites with inorganic slabs derived from the (110) and (111) crystallographic planes of the 3D single perovskite structure are well-known.[69] However, to date, there are no examples of (110) double perovskites. Likewise, while the K2PtCl6-type perovskites belong to the (111) family (see Section 2.3, Figure 4D),[69] these materials do not qualify as dimensionally reduced double perovskites because we consider relatively undistorted vacancies to be distinct [BX6]4− motifs that should be included when evaluating the structural connectivity. The perovskite Cs4Cu6Sb6Cl12, which consists of (111) layers of three chemically different ordered [BX6]4− motifs ([CuCl6]4−, [SbCl6]4−, and [[Cl]6]4−)[70] also does not fit our definition of a dimensionally reduced double perovskite. The unreported (110) and (111) families of dimensionally reduced halide double perovskites (Figure 5B,C) present intriguing synthetic targets, which may exhibit properties quite different from their (001) counterparts, as shown for the lead-halide single perovskites.[73]

2.5. Structural Distortions

Structural distortions of the perovskite framework are well-known to have important consequences for a material’s optical and electronic properties.[70] In the following sections, we discuss structural distortions found in halide double perovskites.

2.5.1. Structural Distortions of Elpasolites

Theoretically, double perovskites can undergo many different tilting distortions, as studied in detail by Woodward and co-workers.[77] However, nearly all elpasolites with X=Cl−, Br−, I− belong to the cubic space group Fm.3m at room temperature and, thus, exhibit perfect octahedral coordination of the B-site cations and no octahedral rotation. Notable exceptions include tetragonal Cs2Au'Au''X6 (X=Cl−, Br−, I−).[73] and Cs2HgPdCl6,[68] (in which the B and B' centers adopt linear and square-planar geometries, respectively), rhombohedral (MA)2KBiCl6 (with room-temperature B-X-B' bond angles differing from 180°),[78] and several halide cryolites (a subset of the elpasolites with the general formula A1+2A'B'X6) including Na2NaGaBr6.[69] Indeed, both octahedral distortions and tilting are observed in the halide cryolite family, which consists mostly of fluorides.[80] Theoretically, double perovskites can undergo many different tilting distortions, as studied in detail by Woodward and co-workers.[77] However, nearly all elpasolites with X=Cl−, Br−, I− belong to the cubic space group Fm.3m at room temperature and, thus, exhibit perfect octahedral coordination of the B-site cations and no octahedral rotation. Notable exceptions include tetragonal Cs2Au'Au''X6 (X=Cl−, Br−, I−).[73] and Cs2HgPdCl6,[68] (in which the B and B' centers adopt linear and square-planar geometries, respectively), rhombohedral (MA)2KBiCl6 (with room-temperature B-X-B' bond angles differing from 180°),[78] and several halide cryolites (a subset of the elpasolites with the general formula A1+2A'B'X6) including Na2NaGaBr6.[69] Indeed, both octahedral distortions and tilting are observed in the halide cryolite family, which consists mostly of fluorides.[80]

2.5.2. Octahedral Rotations in K2PtCl6-Type Perovskites

The B-site vacancy in K2PtCl6-type perovskites decreases the rigidity of the 3D framework, enabling greater rotational freedom of the [BX6]4− octahedra and a larger diversity of A-site cations. Undistorted octahedral coordination of the B+ cation is maintained in lower-symmetry K2PtCl6-type perovskite structures, where either oversized[81] or undersized A-site cations (see list compiled by Brown[22]) induce octahedral tilting. We consider these non-cubic materials to be double perovskites only if the vacancy coordination resembles an octahedron (see Section 1.1). This definition is subjective; we expect that future experimental work will elucidate the maximum possible degree of distortion at the vacancies that still maintains the properties of a double perovskite. Besides these static distortions, anharmonic lattice dynamics, similar to those studied in single perovskites,[82] are widely reported in K2PtCl6-type perovskites[83] and are discussed elsewhere in more detail.[68b] As one example, the coupling of cesium displacements with octahedral rotations breaks the harmonic behavior of vibrations in both CsSnIII3I6[82a] and Cs2SnIVI6[84] thus illustrating the generality of structural phenomena in single and double perovskites.

2.5.3. Distortions in 2D Double Perovskites

All 2D halide double perovskites reported to date exhibit significant local structural distortions,[34,62a–d,73] likely enabled by the enhanced structural flexibility afforded by the 2D framework relative to the 3D framework. The strict geometrical constraints imposed by the 3D perovskite structure are much less important in 2D structures, enabling the [BX6]4− units to distort and tilt to achieve a more stable arrangement. Indeed, several reported 2D double perovskite compositions have not yet been realized in a 3D framework.[68b–d] For example, the instability of CuI-based 3D double perovskites, such as the hypothetical A3CuInX6, has been attributed to the preference of CuI for three- or fourfold coordination.[85] but several examples of CuI-based 2D double perovskites have recently emerged where the CuI centers adopt extremely distorted sixfold coordination spheres while still maintaining the perovskite structure (Figure 6C).[62d,72] The templating effect of the organic cations has also been implicated in directing the self-assembly of several distorted 2D double perovskite compositions,[62d,72] similar to templating effects well-known in 2D halide single perovskites.[69]

3. Electronic Structure

In the following sections, we discuss why double perovskites show a wider diversity of band structures than single perovskites, outline a simple and intuitive model for understanding and predicting their electronic structures, and highlight how symmetry-forbidden band gaps arise. An accessible introduction to band diagrams and reciprocal space by Hoffmann may prove useful to researchers unfamiliar with these topics.[86]

3.1. Implications of Broken B-Site Symmetry

In both single and double perovskites, the A-site cation typically does not directly contribute its orbitals to the valence band (VB) and conduction band (CB) electronic states.[85,87] In single perovskites, this leaves the [BX6]4− unit as...
the fundamental building block of the material’s electronic states,[87] whereas the electronic structure in double perovskites is constructed from the combination of \[\text{BX}_6\] and \[\text{B'}X_6\] units.[9] This broken B-site symmetry leads to significantly more possible electronic structures for double perovskites compared to single perovskites.

In addition to creating a larger variety of electronic structures, the broken B-site symmetry can also fundamentally change the nature of the band-edge optical transition in double perovskites. In the well-studied lead-halide perovskites, the band gap can be viewed as a ligand-to-metal charge-transfer (LMCT) transition between halide p-orbital-dominated states in the VB (albeit with Pb s-orbital character) to Pb p-orbital-dominated states in the CB.[88] Similar LMCT band gaps occur in some double perovskites, particularly the \(\text{K}_2\text{PtCl}_6\)-type perovskites.[7b,9,61a,c,89] However, for many elpasolites, the band-edge transition has significant metal-to-metal charge-transfer (MMCT) character.[9] In the early literature, the jet black color and polarization-dependent absorption spectra of mixed-valence gold double perovskites were attributed to a \(\text{Au}^{I} \rightarrow \text{Au}^{III}\) intervalence charge transfer (IVCT).[28c] More recently, our work on the double perovskites \(\text{Cs}_2\text{AgInBr}_7\), \(\text{Cs}_2\text{AgInCl}_7\), and \(\text{Cs}_2\text{AgTlBr}_8\) showed that the VB states have a large degree of \(\text{Ag}^{+}\) d character and the CB states have significant \(\text{Tl}^{3+}\) s character. As a consequence of the relatively small difference in energy between the \([\text{AgX}_6]^{5-}\) HOMO and \([\text{TiX}_6]^{3-}\) LUMO, the MMCT nature of the band gap results in an abnormally small band gap of 0.95 eV for \(\text{X} = \text{Br}^{-}\) (2.0 eV for \(\text{X} = \text{Cl}^{-}\)).[30] Tuning this MMCT transition in elpasolites through proper selection of B/B' combinations offers a powerful way to control the band gap.[54]

### 3.2. Predictions of the Electronic Structure from Orbital Symmetry

Seeking a chemically intuitive interpretation of double perovskite band structures, our group developed a qualitative linear combination of atomic orbitals (LCAO) framework.[9] Using this approach, a qualitatively accurate band structure of nearly every known halide double perovskite can be determined by considering only the bonding and antibonding interactions between nearest neighbors (B-X interactions) and next-nearest neighbors (interactions between halides at right angles from one another within the same octahedron). The positions of the valence band maximum (VBM) and conduction band minimum (CBM) depend strongly on the match or mismatch in symmetry between the B and B' frontier atomic orbitals. Isoelectronic combinations of B and B' cations give rise to direct band gaps, whereas other B and B' combinations can produce either indirect or direct band gaps. Overall, this LCAO model allows prediction of the VBM and CBM of a double perovskite, often from its chemical formula alone (Table 1).

### 3.3. Symmetry-Forbidden Band Gaps

Analogous to molecular transitions, the absorption of light by centrosymmetric solids obeys the Laporte selection rule.[89] Thus, optical transitions between states with identical inversion symmetry (e.g. \(E_g\) and \(A_{1g}\)) are symmetry-forbidden (also called Laporte- or parity-forbidden), leading to weak optical absorption (Figure 7 A).[90] Yan and co-workers have...
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Double perovskites are very tolerant hosts for impurity alloying, and the effects of substoichiometric substitution of a range of different B-site cations have been explored. In isovalent alloys, in which the impurity cation replaces a cation of the same charge, stable solid solutions generally form across most or all of the composition range. In aliovalent alloys, introducing dopants often generates cation vacancies (such as Ag⁺ vacancies) because of the charge mismatch between the impurity cation and the cation it replaces. This limits the range of achievable compositions to low dopant concentrations (typically <1 atom%).

However, substitution of Sn⁴⁺ cations in Cs₂SnCl₆ by equal amounts of Sb⁵⁺ and Sb⁵⁺ demonstrates that, in some cases, formation of charge-compensating vacancies can be avoided in aliovalent alloys, thus affording greater compositional flexibility. Nevertheless, even at impurity concentrations as low as 1 atom%, both iso- and aliovalent alloying can dramatically modify the size and symmetry of the host material’s band gap.

Isoelectronic alloys involve substitution of a cation in the host structure by an impurity cation that has the same electronic configuration. Thus, a change in the size and shape of the band gap is not expected (see Section 3.2), only a modification of its size. For example, in Cs₂Ag(Bi,Listl)Br₆ the band gap drops gradually with increasing Sb⁵⁺ substitution, but remains indirect throughout.

Figure 8. Schematic band diagram showing the change in electronic structure over the composition range of the Cs₂Ag(Bi₁ₓTlx)Br₆ solution. Only the bands or portions of bands that change on alloying are colored. The red and blue lines correspond to the bands of Cs₂AgBiBr₆ and Cs₂AgTlBr₆, respectively, while purple shows an intermediate composition. Horizontal dashed black lines show the approximate energies of the isolated molecular orbitals.

4.1. Alloying

4.2. Dimensional Reduction

Dimensional reduction is a powerful handle for tuning electronic structures, however, the electronic effects of the dimensional reduction of halide double perovskites have only recently been explored. In the first study on this topic, we reported that the indirect band gap of 3D Cs₂AgBiBr₆ is maintained in all materials with \( n \geq 2 \) but becomes direct in the \( n \leq 1 \) perovskite. Calculations on the band structure of undistorted model systems indicated that dimensional reduction drives this band-gap transition, although local structural distortions of the perovskite framework modulate band dispersion. Since this work, several additional studies of 2D double perovskite electronic structures have emerged. In particular, our work on the electronically distinct Ag-Tl family of halide double perovskites demonstrates that dimensional reduction drives an analogous direct-to-indirect band-gap transition at the \( n = 1 \) limit of Cs₂AgTlBr₆. This substantial change in the electronic structure observed at the \( n = 1 \) limit in two electronically distinct double perovskite families is intriguing, and understanding the generality of this transition across the wide array of possible compositions is a worthy topic for future research.
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transformation of Cs₅PdIVI₆ to Cs₂PdIII₄I₂ demonstrates interchangeable coordination from square-planar [PdI₄]⁻ to octahedral [PdI₄]₃⁻.[105] Although interoctahedral interactions in K₂PtCl₆-type perovskites are historically disregarded,[106] recent work illustrates that interactions across the vacancies, particularly in iodide perovskites, generate dispersed CBs.[107] Moving forward, it is worth developing a more nuanced understanding of interoctahedral interactions in K₂PtCl₆-type perovskites, which exist on the conceptual border between molecular salts with localized orbitals and semiconductors with delocalized bands.

5.4. Other Perovskites

While seemingly trivial, we must not lose sight of the fact that both oxide double perovskites and halide single perovskites boast structure types not yet observed in halide double perovskites. As illustrated by Cs₂NaBiCl₆ (Figure 9 C),[106] halide double perovskites exhibit rock salt B-site ordering. Oxide double perovskites display B-site orderings unknown in the halides (see Section 2.2).[8a, b, 67] and diverse structural topologies exist for lower-dimensional halide single perovskites that remain unknown in the double perovskites (see Section 2.4).[63a] Such materials represent worthy synthetic targets that may afford novel properties.

5.5. Applications

Although this Minireview is focused on fundamental studies, we note that 3D double perovskites have previously been considered for applications in lasing,[27a, b] scintillation,[27c] and upconversion.[27d, 48] More recently, 3D double perovskites have been considered as components of electro-luminescent devices,[7a] X-ray detectors,[7d, 107] and solar cells as absorbers,[52, 53] and preparing thick, high-quality films of these quaternary compounds remains a challenge. Recent studies also show that long carrier diffusion lengths (ca. 11 μm) may be realized in Cs₂AgBiBr₆, if surface trap states are passivated,[93] thus motivating studies on the defect chemistry of double perovskites.

The stunning diversity of chemical compositions and electronic structures afforded by the two distinct B sites of double perovskites brings with it a mighty challenge: can we predict which B-site combinations will provide the desired properties? Despite their long history, foundational studies on halide double perovskites are still needed for us to shrewdly place our bets and win, as the stakes are doubled.

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Conflict of interest

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Two B sites in combination dictate the properties of halide double perovskites (A\textsubscript{2}BB\textsuperscript{′}X\textsubscript{6}; A = monocation, X = halide). This Minireview gives a brief overview of the rich history of halide double perovskites, highlights key structural and electronic aspects, and describes the current understanding on how to correctly select the B-site pairs that afford the desired properties.