Efficient Lone-Pair-Driven Luminescence: Structure–Property Relationships in Emissive 5s\(^2\) Metal Halides

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ABSTRACT: Low-dimensional metal halides have been the focus of intense investigations in recent years following the success of hybrid lead halide perovskites as optoelectronic materials. In particular, the light emission of low-dimensional halides based on the 5s\(^2\) cations Sn\(^{2+}\) and Sb\(^{3+}\) has found utility in a variety of applications complementary to those of the three-dimensional halide perovskites because of its unusual properties such as broadband character and highly temperature-dependent lifetime. These properties derive from the exceptional chemistry of the 5s\(^2\) lone pair, but the terminology and explanations given for such emission vary widely, hampering efforts to build a cohesive understanding of these materials that would lead to the development of efficient optoelectronic devices. In this Perspective, we provide a structural overview of these materials with a focus on the dynamics driven by the stereoactivity of the 5s\(^2\) lone pair to identify the structural features that enable strong emission. We unite the different theoretical models that have been able to explain the success of these bright 5s\(^2\) emission centers into a cohesive framework, which is then applied to the array of compounds recently developed by our group and other researchers, demonstrating its utility and generating a holistic picture of the field from the point of view of a materials chemist. We highlight those state-of-the-art materials and applications that demonstrate the unique capabilities of these versatile emissive centers and identify promising future directions in the field of low-dimensional 5s\(^2\) metal halides.
choices of compatible cations (organic and inorganic) generate an impressive array of structure types (Figure 1), described further below.

The varied dimensionalities of metal halide perovskites give rise to a plethora of different properties deriving from the disruption of the 3D perovskite framework. These dimensionalities range from 0D to 3D, offering a diverse array of applications in different fields.

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Disruption of the 3D perovskite framework. For example, in 2D hybrid perovskites, the alternating organic—inorganic layers lead to anisotropic charge transport and dramatic enhancements in the exciton binding energy due to dielectric confinement. Compositional tuning is similarly critical. For example, the importance of electronic dimensionality has been demonstrated in the double perovskites, which often behave similarly to 0D systems despite their 3D crystal structure.

The structural confinement found in low-dimensional metal halides generates vastly different properties compared with their 3D counterparts, in particular with regard to the mechanism for light emission. Low dimensionality tends to favor the formation of self-trapped excitons (STEs), the recombination of which yields broadband photoluminescence (PL) with generally longer lifetimes. The emission of related compounds has also been interpreted using the frameworks of ion emission, atomic orbital theory, and dielectric confinement. Recent work has begun to realize the potential of these low-dimensional metal halides for a variety of applications complementary to the solar cells and narrow emitters of the 3D halide perovskites, namely, in solid-state lighting, X-ray scintillation, and remote thermometry.

Of these, the highest photoluminescence quantum yields (PLQYs) at room temperature (RT) have been based on Sn2+ or Sb3+ cations containing the active 5s2 lone pair. In this Perspective, we seek to provide insight into the structure—property relationships that dictate the performance of low-dimensional, emissive 5s2 materials. While the focus here is on 0D compounds, there is a rich chemistry of these materials that has not been fully explored for light emission, and thus, we begin with a structural overview. In particular, we highlight the stereoreactive effects of the 5s2 lone pair, which generates the appropriate atomic environments for such emission, and unify the language used to describe this emission by considering the terminologies of ion emission, the atomic orbital approach, and the self-trapped exciton model. We believe that this burgeoning field will benefit from a common mechanistic understanding and a summary of the available structure types that exhibit broadband emission.

**DIMENSIONALITY AND EMISSION IN OCTAHEDRAL METAL HALIDES**

Here a brief introduction to dimensional reduction of metal halides is given through the series of perovskite-derivative structures based largely on corner-connected octahedral metal cations (Figure 1). The varied dimensionalities of metal halide perovskites give rise to a plethora of different properties deriving from the disruption of the 3D perovskite framework.

**Figure 1. Structural versatility of octahedral metal halides: dimensional reduction of the aristotypical AMX3, 3D perovskite to low-dimensional metal halides.**

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excitons at room temperature, causing bulk (100) 2D perovskites to emit more efficiently at room temperature.\(^{34}\) Broad emission from STEs is common at low temperatures but requires structural distortion of the Pb–X–Pb angle to manifest at room temperature,\(^{26}\) so free exciton emission is most common in the (100) 2D perovskites. The (110)-type 2D perovskites possess further anisotropy, as corner-sharing occurs in a straight line along one direction while the other direction has zig-zag chains that disrupt charge transport within the inorganic layer, providing further confinement.\(^{53,56}\) In some sense, the (110) 2D perovskites share more similarities to one-dimensional (1D) perovskites than to their (100) or 3D counterparts, and accordingly, the emission properties of these materials are drastically different, with the manifestation of RT STE emission in (110) perovskites.\(^{56,57,58}\) This class represents an edge case in this regard, as it includes several (110) compositions exhibiting both free exciton and STE emission.\(^{56,56}\)

2D defect perovskites formed from trivalent cations (e.g., Sb\(^{3+}\) or Bi\(^{3+}\)) must balance the excess charge on the M site with one-third occupancy of vacancies; this yields the formula A\(_2\)M\(_2\)□X\(_3\) (where □ represents a vacancy) and forms bilayers cut along the (111) direction of the 3D perovskite (Figure 1).\(^{59,60}\) It should be noted that the (111) direction of the 3D perovskite corresponds to the R symmetry point of the Brillouin zone, where the band edge states lie, and thus, the 2D defect perovskite most effectively breaks up the 3D perovskite. Furthermore, while this structure maintains 2D hexagonal symmetry within the octahedral layer, it is further removed from the 3D perovskite than the (100) or (110) 2D perovskites because no straight lines connect more than two octahedra.\(^{61}\) Accordingly, these compounds exhibit STEs and relatively poor charge transport properties compared with either 3D or (100) 2D perovskites.\(^{14,61,62}\) For further information on 2D perovskites, we refer the reader to recent reviews that describe these compounds in greater detail.\(^{50,51}\)

Further reducing the dimensionality to 1D compounds begets wholly different properties compared with the 3D perovskites because of the limitation of orbital overlap to a single crystallographic axis. While there are a variety of corner-connected octahedral structures ranging from straight trans-connected chains to zigzag cis-connected chains (Figure 1)\(^{63}\) and corrugated double chains,\(^{64}\) their optical properties are relatively unexplored. The corrugated compounds Cs\(_3\)M\(_2\)Cl\(_9\) (M = Sb, Bi) are known to be emissive at low temperatures only,\(^{65}\) whereas efficient STE emission from 1D metal halides has been obtained from edge-shared double chains.\(^{66}\)

0D metal halides possess fully isolated octahedral units, which can be bridged by inorganic cations as in Cs\(_5\)SnBr\(_{14}\) or large organic cations as in (C\(_{4}\)N\(_{2}\)H\(_{14}\)Br\(_{2}\))\(_2\)SnBr\(_{6}\).\(^{19,57}\) While corner-connected octahedra form many higher-dimensional frameworks, corner-connected 0D clusters are quite rare: no divalent cations exhibit such anions, while only seven compounds are known to exhibit emission at room temperature marked in green. The coordinative flexibility of 0D units permits a wide range of structures, many of which possess emission at room temperature. It should be noted that the table is limited to dimeric units for clarity and that a variety of polynuclear 0D compounds exist beyond those listed.\(^{33,44,57}\)

### 0D Units and Chemistry of the 5s\(^2\) Lone Pair

In addition to octahedral units, ns\(^2\) metal halides can form structures based on pyramidal MX\(_3\) units, disphenoidal MX\(_4\) units, and square-pyramidal MX\(_5\) coordination (Figure 2).\(^{31,43}\)

#### 0D Unit Lone Pair Expression

\[
\begin{align*}
\text{MX}_3 & \quad \text{MX}_4 \\
\text{MX}_5 & \quad \text{MX}_6
\end{align*}
\]

**Figure 2. Atomic environments of 0D ns\(^2\) metal halides, with the lone pair visualized in orange.**

which can be built into polymeric frameworks and chains just as in the case of the octahedral metal halides.\(^{13,60}\) The increasing structural diversity with reduced dimensionality is illustrated in Table 1 for 5s\(^2\)-based metal halides (Sn\(^{2+}\), Sb\(^{3+}\)), with archetypes known to exhibit emission at room temperature.\(^{33,44,57}\) The table is limited to dimeric units for clarity and that a variety of polynuclear 0D compounds exist beyond those listed.\(^{33,44,57}\)

#### Table 1. Anionic 5s\(^2\) Metal Halide Structural Units

| X/M | 0D | 1D | 2D |
|-----|----|----|----|
| 2.5 | [SnX\(_3\)]\(^-\) | 71 | [SnX\(_3\)]\(^-\) | 70 |
| 3.5 | [SnX\(_3\)]\(^-\) | 72 | [SnX\(_3\)]\(^-\) | 73 |
| 4  | [SnX\(_3\)]\(^-\) | 74 | [SnX\(_3\)]\(^-\) | 76 |
| 4.5 | [SbX\(_4\)]\(^-\) | 77 | [SbX\(_4\)]\(^-\) | 79 |
| 5  | [SbCl\(_4\)]\(^-\) | 80 | [SbCl\(_4\)]\(^-\) | 83 |
| 5.5 | [SbX\(_5\)]\(^-\) | 84 | [SbX\(_5\)]\(^-\) | 86 |
| 6  | [SbX\(_5\)]\(^-\) | 88 | [SbX\(_5\)]\(^-\) | 90 |

**Table 1. Anionic 5s\(^2\) Metal Halide Structural Units**

**Compounds with room-temperature emission shown in green.**

[https://dx.doi.org/10.1021/acsmaterialslett.0c00211](https://dx.doi.org/10.1021/acsmaterialslett.0c00211)
The coordinative flexibility of 0D units permits a wide range of structures, many of which possess emission at room temperature.

Excited states play a critical role in the optoelectronic properties of metal halides, and in these 0D complexes the geometry is dictated by the outer-shell ns2 lone pair electrons. Hence, it is helpful to visualize the stereochemistry of the lone pair in each coordination environment, shown in orange in Figure 2. The lone pair induces a statically expressed distortion in these units, from the expected trigonal-planar to trigonal-pyramidal in MX3 anions, tetragonal to disphenoidal in MX4 anions, and trigonal-bipyr amidal to square-pyramidal in MX6. In contrast, the octahedral MX6 anion can be found in either inert crystallographic environments, where the site symmetry is essentially cubic, or in environments where the lone pair is expressed through a trigonal or tetragonal deformation. Intriguingly, even the inert MX6 octahedron exhibits some tendency toward off-centering, with signs of dynamic excited-state structural fluctuations observed in tellurium halides and Cs4MX6. The importance of such features in the optical performance will be discussed for the case of 5s2 metal halides based on Sn2+ and Sn3+.

The 5s2 lone pair has an exceptionally rich chemistry because of the combination of stereoactivity and structural flexibility compared with neighboring metals. Following the inert pair effect, the oxidative stability of ns2 cations increases moving down the periodic table, with 6s2 cations such as Pb2+ and Bi3+ having the most chemically inert lone pairs. Lone pair electrons have strong stereochemical effects on the metal–ligand coordination environment; however, this lone pair expression is distinct from the chemical stability of the “inert” lone pair. The same larger 6s2 cations offer more space for the lone pair and reduced surface charge density on the cation than their lighter neighbors, increasing the polarizability and coordination number. These features permit structurally inert lone pairs such as the highly symmetric structures of PbI2 and BiI3, which have centered metal cations with no obvious lone pairs such as the highly symmetric structures of PbI2 and PbBr2 because of the combination of stereochemical influence of its lone pair electrons with the appropriate size disparity between the metal and halogen, despite the fact that SnCl2 exhibits the strongest repulsion of the lone pair. Similarly, while BiI3 adopts a layered structure with perfectly symmetric [BiI4]3− octahedra, BiCl3 exhibits trigonal distortions that lead to pyramidal coordination, requiring additional crystal forces to return to the high-symmetry octahedra of CsBiCl6. The smaller size of Sb causes all three binary halides SbX3 (X = Cl, Br, I) to exhibit such off-centering, but the templating influence of other cations can enforce high-symmetry crystallographic sites such as the [SbCl6]3− octahedra in Rb-SbCl6 and Cs2NaSbCl6. The case of Cs2NaSbCl6 is especially interesting, as the enforced octahedral symmetry on a normally expressed SbCl3 lone pair leads to a large lattice constant of 10.7780 Å for Cs2NaSbCl6 while that of the isostructural Cs2NaInCl6 is 10.5313 Å, despite the similar ionic radii of Sb3+ and In3+ (0.76 vs 0.80 Å). This points to a dynamic distortion of the [SbCl6]3− octahedron in which the stereochemistry of the lone pair is expressed dynamically while the cubic-long-range symmetry is maintained. However, this does not occur in the isostructural Cs2NaSbBr6, in which the ionic radius is consistent with the expected value, highlighting the importance of metal–halogen overlap in determining the dynamics of the lone pair.

The contrast of lone pair stability and expression makes the 5s2 lone pair unique, as it lies on the cusp between the dynamically expressed lone pairs of 6s2 cations and the statically expressed lone pairs of the 4s2 cations.

This highlights that lone pair expression is also heavily influenced by the halogen size. For example, the binary halide SnBr2 exhibits a different structure than SnCl2, SnI2, PbCl2, and PbBr2 because of the combination of stereochemical influence of its lone pair electrons with the appropriate size disparity between the metal and halogen, despite the fact that SnCl2 exhibits the strongest repulsion of the lone pair. Similarly, while BiI3 adopts a layered structure with perfectly symmetric [BiI4]3− octahedra, BiCl3 exhibits trigonal distortions that lead to pyramidal coordination, requiring additional crystal forces to return to the high-symmetry octahedra of CsBiCl6. The smaller size of Sb causes all three binary halides SbX3 (X = Cl, Br, I) to exhibit such off-centering, but the templating influence of other cations can enforce high-symmetry crystallographic sites such as the [SbCl6]3− octahedra in Rb-SbCl6 and Cs2NaSbCl6. The case of Cs2NaSbCl6 is especially interesting, as the enforced octahedral symmetry on a normally expressed SbCl3 lone pair leads to a large lattice constant of 10.7780 Å for Cs2NaSbCl6 while that of the isostructural Cs2NaInCl6 is 10.5313 Å, despite the similar ionic radii of Sb3+ and In3+ (0.76 vs 0.80 Å). This points to a dynamic distortion of the [SbCl6]3− octahedron in which the stereochemistry of the lone pair is expressed dynamically while the cubic-long-range symmetry is maintained. However, this does not occur in the isostructural Cs2NaSbBr6, in which the ionic radius is consistent with the expected value, highlighting the importance of metal–halogen overlap in determining the dynamics of the lone pair.

The contrast of lone pair stability and expression makes the 5s2 lone pair unique, as it lies on the cusp between the dynamically expressed lone pairs of 6s2 cations and the statically expressed lone pairs of the 4s2 cations. This interplay of dynamic and static off-centering is at its peak in the 0D 5s2 metal halides, permitting structural distortions that can yield efficient luminescence in materials where similar 4s2 or 6s2 structures have nonexistent or weak emission. For example, while Cs3PbBr6 does not emit at room temperature, Cs3SnBr6 and (C6H5)4SnBr4 have bright emission with PLQYs of 15% and 95%, respectively. This can be understood as a function of the enhanced hybridization between the metal ns2 lone pair and the halide np orbitals, with recent work showing that the higher energy of the Sn ns level leads to the trend Cs3SnBr6 > Cs2SnI6 > Cs3PbBr6 favoring efficient STF emission in the former while the latter only emits at low temperatures. Similarly, in the disphenoidal metal bromides (bmpip)4MBr4 (bmpip)4SnBr4 has a PLQY of 75%, while that of (bmpip)4PbBr4 is only 24% and that of (bmpip)4GeBr4 is below 1%. To better understand the broad, bright luminescence driven by the 0D 5s2 lone pair, we bridge together the various models that have been utilized to characterize this emission.
UNIFYING THEORY OF 5s² EMISSION

Emission from the isolated center can manifest itself in many different forms, e.g., a dopant in a host matrix or pure material, as well as under different conditions, e.g., cryogenic or room temperature. Researchers from different fields of spectroscopy and materials science have contributed to isolated center emission studies. Because of this, different theoretical models are circulating in the literature. While these models share many features, the absence of a unified model (or the discussion of such a model) leads to contradicting and confusing terminology. Here we attempt to bring together the important theoretical concepts into a unified framework.

Two main models are presently utilized, arising from either (1) treating 0D centers as isolated ions dressed in the halide ligand field or (2) presenting these as the limiting case of complete electronic and structural isolation in the framework of an extended solid. Overall, both approaches lead to the same theoretical picture of the isolated MX₅ centers, as illustrated in Figure 3A. Unification of the two models provides a framework that can explain and predict many properties of emissive 0D metal halides.

The first theoretical description is derived from the simple two-electron Seitz model (Figure 3B). In this model, a free ion with the ns² configuration has the singlet electronic ground state, denoted with atomic term symbol ¹S₀. The splitting of the nsnp excited states into ¹P (singlet) and ³P (triplet) states occurs as a result of the Coulomb (F) and exchange (G) interactions. Further, the ³P states are split into non-degenerate states ³P₂, ³P₁, and ³P₀ by the spin–orbit coupling interaction. Additionally, the overall energy of all of the described states is non-uniformly altered by the ligand field (in this case by the coordinating halides). This interaction with the ligand field for ns² ions includes a large degree of hybridization between the atomic orbitals of the central metal and ligands, which is described by molecular orbital (MO) theory (Figure 3C). In this case, the ground and excited states are localized on both central ions and...
ligands. Atomic term symbols in this description are substituted with molecular term symbols (i.e., \(^1S_0\) becomes \(a_0\)). The relative energy of the latter depends directly on the molecular geometry (i.e., octahedral, square-pyramidal, disphenoidal) and has been summarized by Vogler and Nikol for different possible molecular geometries.\(^{31}\) However, it remains very common in the literature to use atomic term symbols even for systems with a high degree of hybridization and denote the resulting molecular states as \(^1P_1\)-derived, \(^3P_0\)-derived, etc.\(^{38,106,107}\) In this way, the model still serves its main purpose: to explain the transitions that occur between the states in terms of their allowed or forbidden nature, which can be experimentally reflected in the measured emission decay time (i.e., longer radiative lifetimes for partially forbidden transitions and shorter for allowed ones) or the intensity of the corresponding excitation band.\(^{30,108}\)

For example, the dramatic reduction of the radiative lifetime of \(Cs_2NaSbCl_6\) from 1.4 ms at 5 K to 0.15 \(\mu\)s at higher temperatures with no change in the emission intensity until \(\sim 200\) K is entirely derived from changes in the character of the radiative excited state, from the forbidden \(^3P_0\) \(\rightarrow \)^1S_0\) transition to low temperatures to the \(^3P_1\) \(\rightarrow \)^1S_0\) transition by \(\sim 25\) K.\(^{29}\) On the other hand, the MO approach becomes useful for comparing optical properties for different geometries as well as correctly predicting the ground- and excited-state geometries. This is especially crucial for these 0D systems in which the halide bonds are not shared, and thus, the metal halide anion and its lone pair are free to distort in the excited state, and the excited-state geometry is dramatically different than the ground-state geometry.

Historically, the Seitz model was widely used to interpret the optical properties of ns\(^2\) ion impurities in binary alkali metal halides\(^{169}\) or in various other oxide and halide hosts.\(^{29,30}\) The STE model for interpretation of the optical properties of 0D metal halides became widespread only recently because of the research focus on ns\(^2\) metal halide semiconductors. While free excitons are dominant in the prototypical 3D AMX\(_3\) semiconductors, the structural versatility of metal halides yields many compounds where STEs dominate.\(^{50}\)

The typical theoretical description of phonon-assisted STE recombination involves a single configurational coordinate (SCC) diagram, in which the abscissa represents a change in molecular geometry upon excitation (\(Q\)) and the ordinate represents a change in energy (Figure 3D).\(^{110}\) Ground and excited states in this model are described as parabolic potential energy functions, which are harmonic in the first approximation. It should be noted that in this SCC diagram, the free exciton excited state would be represented as a parabola centered at the ground state with higher energy;\(^{24}\) however, free excitons have not been observed in 0D Ss\(^2\) metal halides, and hence, our model considers the localized self-trapped exciton as the only stable excited state. This is consistent with the description of Ueta et al., demonstrating that 1D or lower-dimensional systems have unstable free exciton states that localize upon any perturbation,\(^{24}\) which means that the self-trapped exciton is the only relevant state in 0D Ss\(^2\) metal halides. This simplifies the STE model to an SCC diagram essentially identical to the generalized vibronic transitions described by the Franck–Condon principle. Here we maintain the use of the term “self-trapped exciton” to be consistent with the literature on higher-dimensional metal halides.

The minimum of each parabola represents the equilibrium geometry of the ground or excited state, while the horizontal difference between these geometries, \(\Delta Q\), is interpreted as the structural change that the metal halide center undergoes upon excitation. The difference between the excited- and ground-state geometries is reflected in the large Stokes shift of 0D Ss\(^2\) metal halide emission. Both absorption and emission transitions can occur from different vibronic states (denoted as flat lines in the parabola), thus yielding an amalgam of individual transitions with emission probabilities following a Poisson distribution. The convolution of these transitions results in a broadened emission peak, often with a tail toward lower energy.\(^{25}\) The magnitude of the electron–phonon coupling is described by the Huang–Rhys parameter, which is larger for stronger coupling and defines the degree of broadening associated with STE emission.\(^{59,110}\)

The STE model’s configurational coordinate diagram is a simplified projection that represents a complex energy surface as a two-dimensional plot and therefore has limitations, especially in complex materials with multiple emissive centers. However, it has proven quite useful in characterizing STE emitters in recent years,\(^{39,111,112}\) and in conjunction with the Toyozawa model,\(^{24}\) important features such as the Huang–Rhys parameter and effective phonon energy can be derived. Importantly, this model also rationalizes a key property of STE emitters: temperature-dependent emission quenching.\(^{59,108}\) The crossing of the ground- and excited-state parabolas provides a nonradiative relaxation pathway from the excited-state minimum to the crossing point purely through phonon excitation, known as hot nonradiative recombination.\(^{24}\) The energy difference (height) between the intercept and the excited-state minimum defines the energy barrier (and thereby the temperature, as described further below) required to quench the radiative process (Figure 3D).

Thus, the Seitz model mainly focuses on the nature of the electronic states and, with the MO extension, on their degeneracy in the electric field of the ligand, while the SCC model describes phonon–exciton interactions. The successful interpretation of observed phenomena in the optical properties of 0D materials requires the aid of all three theoretical concepts. The unified model is depicted in Figure 3E. It is based on the SCC diagram, where the excited state can be split into several nondegenerate states, each reflecting the nature of the contributing atomic state. As we will show, the splitting and degeneracy of these states vary with the coordination geometry, but this model is flexible enough to describe the observed optical features.

### PROPERTIES OF EMISSIVE Ss\(^2\) 0D MATERIALS

Among the various emissive Ss\(^2\) 0D materials that have been reported, the simplest case with which to study such structure–property relationships comes from Te\(^{4+}\). The high charge of the metal center necessitates a greater number of halide ligands, restricting the known Te\(^{4+}\) halides to materials containing octahedrally coordinated Te\(^{4+}\) regardless of the nature of the counteranion.\(^{87,113}\) The most commonly adopted structure is that of the vacancy-ordered double perovskite \(A_2TeX_6\) with regular octahedra.\(^{87}\) The isostructural nature of these compounds has encouraged excellent fundamental studies; for example, the role of the halide in luminescence quenching has been studied in the series \(Cs_2TeX_6\) and \(A_2TeX_5\) with chlorides showing the brightest emission at RT.\(^{86,88,90,113,115}\) The apparent simplicity of these materials, however, has not been manifested in numerous luminescent examples, as the
quenching temperatures are relatively low in these compounds,\textsuperscript{86} and those that do emit at RT are plagued by low PLQYs. This appears to be due to an apparent concentration quenching effect\textsuperscript{86} that is less pronounced in other 5$s^2$0D metal halides, but the root cause deserves further investigation given the exceptional performance of Sn$^{2+}$ and Sb$^{3+}$ emissive materials and Te$^{4+}$’s distinct advantages of stability and its tendency to adopt a single coordination that encourages rational design.

At the other end of the spectrum, Sn$^{2+}$ with its low charge exhibits the greatest structural diversity of 0D compounds, with examples of luminescent materials containing octahedra, disphenoids, and trigonal pyramids (Table 2 and Figure 4A). Additionally, a 0D structure containing square pyramids (Rb$^+$SnCl$_3$I$_2$) was also recently discovered; however, its potential for luminescence was left unexplored.\textsuperscript{116} Though Sn$^{2+}$ is a versatile ion for materials discovery, its tendency to oxidize to Sn$^{4+}$ increases the synthetic difficulty of discovering new materials.\textsuperscript{117} This may be one of the reasons why so far only seven room-temperature luminescent 0D structures have been

| compound | coordination unit | $E_{\text{exc/abs}}$ (nm) | $E_{\text{em}}$ (nm) | Stokes shift (eV) | FWHM (eV) | PLQY (%) | lifetime ($\mu$s) | ref |
|----------|-------------------|---------------------------|--------------------|-------------------|-----------|---------|-----------------|-----|
| Cs$_4$SnBr$_6$ | MX$_3$ | 340 | 540 | 1.28 | 0.51 | 15 | 0.54 | 37 |
| HDM$_3$SnBr$_8$ | MX$_3$ | 350 | 600 | 1.60 | 0.44 | 86 | 3.12 | 120 |
| (C$_5$N$_4$H$_2$Br)$_3$SnBr$_6$ | MX$_3$ | 355 | 570 | 1.32 | 0.40 | 95 | 2.2 | 19 |
| (PEA)$_2$SnBr$_4$ | MX$_3$ | 340 | 566 | 1.46 | 0.44 | 89.5 | 2.7 | 121 |
| (C$_5$N$_4$H$_2$I)$_4$SnI$_6$ | MX$_3$ | 350 | 658 | 1.66 | 0.37 | 75 | 4 | 34 |
| (C$_5$H$_2$N$_2$I$_2$)$_2$SnCl$_3$ | MX$_3$ | 350 | 638 | 2.48 | 0.42 | 7.6 | 7 | 71 |
| Bzmm$_3$SbCl$_6$ | MX$_3$ | 342 | 525 | 1.26 | 87.5 | 2.4 | 85 |
| Bzmm$_3$SbCl$_6$ | MX$_3$ | 375 | 600 | 1.24 | 22.3 | 2.6 | 85 |
| Bmn$_3$SbCl$_6$ | MX$_3$ | 370 | 583 | 1.22 | 86.3 | 4.26 | 18 |
| (C$_5$NH$_2$)$_3$SbCl$_6$ | MX$_3$ | 380 | 590 | 1.16 | 0.43 | 98 | 4.2 | 19 |
| TTEA$_2$SbCl$_6$ | MX$_3$ | 370 | 625 | 1.37 | 0.45 | 86 | 7.5 | 38 |
| TEB$_2$SbCl$_6$ | MX$_3$ | 360 | 590 | 1.34 | 0.48 | 98 | 7.7 | 38 |
| (Ph$_3$P)$_2$SbCl$_6$ | MX$_3$ | 375 | 648 | 1.39 | 0.41 | 87 | 4.6 | 122 |
| (PPN)$_2$SbCl$_6$ | MX$_3$ | 410 | 635 | 1.07 | 0.44 | 98.1 | 4.1 | 119 |
| Rb$^+$SbCl$_3$$_{10}$ | MX$_3$, M$_2$X$_{10}$ | 365 | 560 | 1.16 | 0.53 | 3.8 | 0.2 | 79 |

Figure 4. (A) 0D structures with statically expressed lone pairs (SnX$_4$, SbX$_5$) and the corresponding energy band diagram. (B) Dynamically distorted octahedral MX$_6$ and the corresponding band diagram. (C) Excitation-dependent PL of (bmpi)$_2$SnBr$_4$ showing singlet and triplet emission.\textsuperscript{34} (D) PL and PL excitation (PLE) spectra of (TTA)$_2$SbCl$_6$ showing the separate excitation of the triplet and singlet states (reproduced using the previously reported synthesis\textsuperscript{38} and characterized using an optical setup described elsewhere\textsuperscript{34}). (E) PL and PLE spectra of Cs$_4$SnBr$_6$,\textsuperscript{37} (C$_5$N$_4$H$_2$Br)$_3$SnBr$_6$,\textsuperscript{19} and [18-crown-6]$_2$Cs$^+$SbBr$_{6}$.\textsuperscript{118}
Some empirical observations lead us to conclude that coordinatively unsaturated metal centers such as SnX4 or MX5 (M = Sn, Sb) can be obtained only through the use of organic and sufficiently bulky counterions or a combination of halides with very different sizes.

From a purely structural perspective, too few structures are known at this point to predict the structure-directing effect that a specific cation may have. However, some empirical observations lead us to conclude that coordinatively unsaturated metal centers such as SnX4 or MX5 (M = Sn, Sb) can be obtained only through the use of (a) organic and sufficiently bulky counterions (e.g., bmpip, PPh4, bzmim, etc.; Table 2) or (b) a combination of halides with very different sizes (e.g., mixed Cl−, I−). Smaller inorganic counterions can enable 0D structures in alkali halide-rich environments that sufficiently isolate the metal halide complex with high coordination numbers (e.g., Cs4SnBr6), but less alkali halide favors the formation of higher-dimensional frameworks (e.g., CsSnBr6), as the small cations cannot fully isolate the 0D units (Table 1).

On the basis of these various Sn2+- and Sb3+-based materials, several examples can be compared to see how the geometry and the metal center affect the resulting optical properties. To examine these differences, the SCC diagrams for 0D Sn and Sb units can be redrawn on the basis of their geometry and the stereoactivity of the lone pair (Figure 4A,B). The “static” lone pair is expressed and found in coordinatively unsaturated geometries such as disphenoids (SnX4) and square pyramids (SnX6) (Figure 4A). In both cases, the reduced symmetry imposed by these motifs results in nondegenerate excited states, which may allow for additional transitions if the energy levels are sufficiently separated, although the separation may be quite small (Figure 4A).

This has been demonstrated by Morad et al., with the observation of both 3P1 → 1S0 and 3P1 → 1S0 transitions at RT in disphenoidal (bmpi)2SbCl5 (Figure 4C). This also highlights the fact that the triplet STE state tends to be the lowest-energy excited state for such 5s2 metals. This same model extends to square-pyramidal Sb (i.e., MX5 in Table 2), for which Wang et al. first observed two distinct emission bands from (bzmim)2SbCl5 and subsequently several other singlet-emitting hybrid antimony chlorides have been found. One such compound is TTA2SbCl5, which further demonstrates the excitation-wavelength-dependent nature of the emission (Figure 4D). High-energy excitation succeeds in populating the high-energy singlet 3P1 state, resulting in emission directly from this state as well as emission from the thermodynamically favored lower-energy 3P1 triplet state.

This situation is simplified in octahedrally coordinated systems (Figure 4B). The larger coordination number reduces the static expression of the lone pair and therefore off-centering and distortion, often leading to high-symmetry sites and similar bond lengths. The regularity (or near-regularity) of such sites obscures the optical properties present in the disphenoidal and square-pyramidal coordinations, as the dynamic distortions of these octahedra lead to stronger mixing of the excited states. This is best illustrated by comparing three 5s2 bromides: Cs5SnBr6, (C6H5)4SnBr4, and [18-crown-6]2Cs3SbBr6 (Figure 4E). Although these three materials have different shifts of the excited state, with 3P1 → 1S0 and 1P1 → 1S0 transitions at RT in disphenoidal (bmpip)2SnBr4 (Figure 4C), this is best illustrated by comparing three 5s2 bromides: Cs5SnBr6, (C6H5)4SnBr4, and [18-crown-6]2Cs3SbBr6 (Figure 4E). Although these three materials have...
different metal centers and different degrees of distortion or lone pair expression, the PL spectra appear to be triplet ($^3P_{0,1,2}$)-dominated with one broad, featureless emission peak. This can be understood in terms of the higher degeneracy of the regular octahedral environment: while the trigonally distorted octahedron would have fully distinct singlet and triplet states, the regular octahedron does not fully separate these levels, and therefore, the singlet remains unobserved. This also correlates with the reduced Stokes shift and emission line width in octahedral compounds relative to their more distorted counterparts; e.g., Vogler and Nikol compared the absorption and emission of disphenoidal SbCl$_6^-$ and octahedral SbCl$_6^{5-}$ in solution.

Given the enormous diversity of structures offered by these Ss$^2$ systems and their recent (re)discovery as optical materials, it is apparent that the community has only scratched the surface concerning their properties and how to utilize them. We highlight two rising applications that take advantage of the unique features of these 0D materials: X-ray scintillation and remote thermometry and thermography.

X-ray scintillation utilizes two features shared by these 0D Ss$^2$ metal halide materials: (1) efficient relaxation processes for high-energy absorption to the STE triplet state and (2) highly Stokes-shifted emission such that the compounds are transparent to their emission. The first such study demonstrated that (bmpip)$_2$SnBr$_4$ could function as an excellent X-ray scintillator (Figure 5A). A very recent work found that square-pyramidal (PPN)$_2$SbCl$_4$ also exhibits efficient X-ray scintillation, and it is likely that many of these materials are radioluminescent. An open question is whether the long emission lifetimes (Table 2) are problematic for X-ray detection. Although these materials have low overall atomic numbers, they still perform comparably to commercially available NaI:Tl or CsI:Tl scintillators and seem to outperform organic scintillators. This class of materials deserves much more investigation in this context, and we hope to see collaborations between traditional scintillator groups and materials chemists to find effective scintillators among the Ss$^2$ metal halides.

The second application, thermometry and thermography, is based on the steep temperature dependence of the PL lifetimes of these materials, as first demonstrated by our group for Cs$_8$SnBr$_6$ (C$_4$N$_2$H$_14$I)$_4$SnI$_6$ and [C(NH$_2$)$_3$]$_2$SnBr$_4$. The PL lifetimes of these compounds vary by up to 2 orders of magnitude over a temperature range of 100 °C, giving rise to some of the highest specific sensitivities among known thermoluminophores. Temperature sensitivity is also observed in the PLQY of many materials, including these, but the dramatic changes in lifetime of 0D Ss$^2$ metal halides impart a much stronger sensitivity than simply utilizing the emission intensity could provide. This property is rationalized by the unified model presented earlier, which is simplified in Figure 5B to highlight the effect of shifting the excited-state parabola. The intersection of two parabolas (colored and black curves) represents a nonradiative pathway back to the ground state. As the Stokes shift increases and the material’s PL red-shifts, the upper excited-state parabola shifts further from the ground-state parabola, lowering the energy barrier $\Delta E$ for the phonon-assisted “hot” nonradiative recombination.

Unlike conventional semiconductors, the PL lifetime in 0D metal halides is intrinsically robust, i.e., without noticeable effects of the structural defects and surfaces. This robust nature is a consequence of the strongly localized excited states of these 0D Ss$^2$ metal halides, which lead to excited-state energy bands with high Stokes shifts and momentum offsets that inhibit nonradiative recombination from defect states and favor hot recombination. The only other known source of nonradiative quenching comes from parasitic impurity phases such as CsSnBr$_6$, which absorbs in the emissive region of Cs$_8$SnBr$_6$ but such quenching is only known to affect the PLQY. Thus, hot nonradiative recombination dominates in 0D Ss$^2$ metal halides, dictated by the energy barrier $\Delta E$ that governs the quenching temperature of the luminescence, $T_{\text{quench}}$. $\Delta E$, along with the average or effective phonon energy, $E_{\text{ph}}$, directly influences the emission lifetime and PLQY through the temperature-dependent competition between the radiative and nonradiative relaxation rates ($k_r$ vs $k_{nr}$, respectively). The onset of quenching, with corresponding changes in lifetime, defines the temperature-sensitive regime. For example, in Figure 5C this regime is found at the higher temperatures, where $k_r$ and $k_{nr}$ compete effectively against one another and $k_r$ remains negligible. In contrast, the flat region at low temperatures (<325 K for (C$_4$N$_2$H$_14$I)$_4$SnI$_6$ <250 K for Cs$_8$SnBr$_6$ and Rb$_7$Sb$_3$Cl$_{16}$) involves a purely radiative process, where $k_{nr}$ is negligible, and the PL lifetime remains rather unleveled and the PLQY is saturated. This trend appears to be general not only for 0D Sn materials but also for 0D Sb materials (Figure 5C). This robust thermal sensitivity, which can be tuned by structural engineering, and the wide temperature and lifetime ranges that it covers make Ss$^2$ metal halides a compelling class of novel thermoluminophores.

Cryogenic temperatures can present exceptions to this behavior that may also prove suitable for thermometric applications, as below 77 K in Rb$_7$Sb$_3$Cl$_{16}$ a second temperature-sensitive regime can be observed without any change in the PLQY. This purely radiative yet thermally sensitive regime is likely driven by changes in the character of the excited-state levels, as described above for Cs$_2$NaSbCl$_6$. The unchanging intensity with concurrent temperature sensitivity ensures that the signal from the thermometric probe will remain strong throughout the entire sensitivity regime. This unique behavior may enable high thermometric sensitivities at extremely low temperatures (below 10–15 K), where accurate temperature values can be difficult to obtain through other means without altering the temperature of the system and hence a simple optical probe may be quite valuable.

### POLYNUCLEAR 0D Ss$^2$ COMPOUNDS

Beyond these isolated 0D units, a plethora of polynuclear 0D cluster compounds based on Ss$^2$ metal cations exist. Their optical potential remains to be thoroughly explored. RT PL has been reported for [Sb$_2$I$_3$]$^{3-}$-dimers in Cs$_8$Sb$_3$I$_6$, but with rather weak emission intensity. This may be due to the asymmetry in these polynuclear systems, which provides stable lone pair off-centering in coupled units that may enhance nonradiative recombination (Figure 6). However, the discovery of Rb$_7$Sb$_3$Cl$_{16}$ and its emissive distorted [Sb$_2$Cl$_9$]$^{3-}$-dimer with a PLQY of 3.8% demonstrates that there are more optically active centers to be discovered. Recent reports on a bright [Pb$_3$Cl$_{11}$]$^{3-}$ cluster with near-unity PLQY provide further encouragement, and we expect emissive clusters to be a rich avenue of exploration moving forward.

### OTHER EMISSIVE METAL CENTERS

We also wish to highlight a recent series of metal halides based on ns$^2$ (d$^{10}$) cations that have exhibited remarkably efficient and

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Polynuclear lone pair expression

Figure 6. Atomic environments of polynuclear 0D 5s^2 metal halides derived from square pyramids and octahedra, with the lone pairs visualized in orange.

broadband luminescence similar to that observed in the 5s^2 metal halides. Examples of nd^{10} emitters have been known for many years among the Cu^+ and Ag^+ halides, but this field has been reinvigorated with a flurry of investigations in the last 5 years showcasing the utility of these materials in scintillators and light-emitting diodes (LEDs). This group has been further bolstered by several new broadband-emissive compounds based on isoelectronic Zn^{2+} and Cd^{2+}. Mixing of nd^{10}ns^2 systems has also led in some cases to enhanced emission, and we expect that there is much more synergy to be found among such mixed-metal systems. In particular, combining the efficient excitation of low-band-gap ns^2-based materials with highly emissive nd^{10} centers could make for attractive white-light phosphors.

In the case of In^{3+}, the reported emission characteristics are extraordinarily similar to those of Sb^{3+}-doped indium halide materials. A new report found that undoped and Sb^{3+}-doped Cs_2InCl_5·H_2O had essentially identical features and temperature-dependent intensities, while recent work in our group showed that pure Cs_2NaInCl_6 and Cs_2InCl_3·H_2O do not emit. In our view, trace Sn^{3+} dopants in the precursors may be responsible for these emissions, similar to the miniscule levels of Sn impurities that were found by Mitzi et al. to generate STE emission in PEA_2PbBr_4. Careful experimental work would be required to demonstrate this, perhaps utilizing InX monohalides as inorganic precursors that would be chemically less likely to contain trace Sn^{3+} impurities. A very recent report further validates this view by demonstrating that pure Cs_2SnCl_6·H_2O does not luminesce without Sn^{3+} doping.

SUMMARY AND OUTLOOK

The future is bright for emissive lone pair materials, and the structural versatility of 5s^2 metal halides yields a wide compositional space for the design of emitters with unique properties. Low-dimensional emissive 5s^2 metal halides offer several advantages: quantum efficiencies near unity; earth-abundant, nontoxic metal cations; intrinsic emission that does not require doping, electronic passivation or particle size control to achieve high performance; and large Stokes shifts that minimize self-absorption. Applications of such compounds include X-ray scintillation, phosphors for white-light emission, and high-resolution thermography, and we expect great strides in each of these fields in the coming years. That being said, challenges persist that will need to be overcome to enable the development of successful devices that fulfill the promise of these applications.

Many open questions deserve further exploration to understand the structure–property relationships and unveil the practical potential of these compounds. At present, it is difficult to predict the coordination environment generated by different organic cations, and finding design principles will require many more examples to tease out the effects of cation size, polarity, bonding characteristics, etc. Even in the absence of such design principles, several important trends can be observed on the basis of the available literature. For example, nearly all examples of highly emissive compounds in Table 2 can be grouped into two kinds, namely, Sn(II) bromides and Sb(III) chlorides, indicating that the orbital overlap and/or phonon energies in these combinations are particularly suited for highly efficient emission. In the Cs_5TeX_6 system, the RT emission intensity increases for lighter halides, similar to Sb(III) halides but contrary to Sn(II) bromides. Further studies, such as the computational comparison of Cs_2SnBr_6, Cs_2SbBr_6, and Cs_2SbBBr_6 that identified the importance of the Sn 5s^2–Br 4p overlap, are needed to determine whether the energy levels of Sn(II) and Br are ideal for efficient emission or whether the lower stability of Sn(II) chlorides is the key to the observed differences. The structural and photophysical aspects of the excited state are rather poorly understood. While we have elaborated on some intriguing trends in the structure–property relationships of these compounds and the connection to the 5s^2 lone pair, a true picture of the dynamics of these systems is currently lacking. Besides the commonplace transient absorption spectroscopy, excited states of these materials can be probed by ultrafast measurements that combine optical excitation and structure probing (ultrafast electron or X-ray scattering).

We also observe that the hybrid organic–inorganic materials routinely exhibit higher PLQYs than their fully inorganic counterparts, which may indicate more effective 0D isolation in the former materials with large and soft organic cations (Table 2). This likely derives from the lower-energy phonons and their enhanced coupling in inorganic materials, whereas the high-energy phonons of the organics improve the structural isolation of the lone-pair-driven vibrational modes in these 0D materials and push the temperature region for thermal quenching to higher temperatures (Figure 5C). However, the inorganic compositions benefit from enhanced stability and higher melting points, as manifested in the ability to prepare nanocrystals (NCs) of Cs_2SnBr_6, which has not yet been demonstrated for any hybrid organic–inorganic 0D compositions.

The properties that allow them to excel as thermosensitive phosphors may hinder the utility of metal halides as solid-state lighting phosphors. During LED operation, the excitation source typically heats the phosphor, with local surface temperatures potentially exceeding 70 °C. While hybrid organic–inorganic metal halides generally exhibit higher PLQYs at ambient and elevated temperatures, their chemical stability becomes a limiting factor. Furthermore, the majority of these materials exhibit excitation peaks below 400 nm, which are unsuitable for use even with purple LEDs (405 nm) and require them to be paired with UV LEDs (for which an inexpensive and
efficient UV light source is unavailable at present) for use as downconversion phosphors in white-light LEDs. The combination of these two limitations necessitates further structural exploration of $\text{Sr}^2$-based materials suitable for white-light LEDs.

With regard to application in scintillators, a pertinent challenge is their intrinsically slow radiative recombination, in the low microsecond range (Table 2). Time-resolved radioluminescence studies are needed to determine the decay time under X-ray excitation and the possibility of afterglow. These compounds may therefore not be suitable for applications that require photon counting and/or spectroscopic X-ray energy resolution capabilities, such as positron emission tomography and nuclear security. However, static X-ray imaging such as used in dental and physician practices would benefit from the low-cost nature of these materials and the high reported sensitivity, which enables a low dose rate to the patient.

So far, we have found that emission characteristics and durability of known $\text{Sr}^2$ metal halides neatly match the theoretical and practical requirements of thermometric applications. The intrinsic nature of the STE emission makes the emission characteristics rather insensitive to the particle size, surface, and common structural defects and hence the synthesis method.

The intrinsic nature of the STE emission makes the emission characteristics rather insensitive to the particle size, surface, and common structural defects and hence the synthesis method. The temperature range of high sensitivity is exceptional and broadly tunable by chemical design, while the respective PL lifetimes lie in convenient ranges for various detection schemes (ns to $\mu$s). Future work should also focus on the design of nanoscopic thermoluminescent probes. This requires the synthesis of size-tunable and environmentally stable nanoparticles of 0D metal halides. For high-resolution thermal imaging of biological systems, these NCs must be water-compatible and water-dispersible.

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**Notes**

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**REFERENCES**

(1) Stoumpos, C. C.; Kanatzidis, M. G. The Renaissance of Halide Perovskites and Their Evolution as Emerging Semiconductors. Acc. Chem. Res. 2015, 48, 2791–2802.

(2) Saparov, B.; Mitzi, D. B. Organic–Inorganic Perovskites: Structural Versatility for Functional Materials Design. Chem. Rev. 2016, 116, 4558–4596.

(3) Miyata, K.; Atallah, T. L.; Zhu, X. Y. Lead halide perovskites: Crystal–liquid duality, phonon glass electron crystals, and large polaron formation. Sci. Adv. 2017, 3, e1701469.

(4) Stoumpos, C. C.; Mallakas, C. D.; Kanatzidis, M. G. Semiconductor Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High mobilities, and Near-Infrared Photoluminescent Properties. Inorg. Chem. 2013, 52, 9019–9038.

(5) Yaffe, O.; Guo, Y.; Tan, L. Z.; Egger, D. A.; Hull, T.; Stoumpos, C. C.; Zheng, F.; Heinz, T. F.; Kronik, L.; Kanatzidis, M. G.; Owen, J. S.; Rappe, A. M.; Pimenta, M. A.; Brus, L. E. Local Polar Fluctuations in Lead Halide Perovskite Crystals. Phys. Rev. Lett. 2017, 118, 136001.
Characterization of Cs₃Sb₂I₉: A Lead-Free Layered Perovskite

Cameron, S.; Hill, I. G.; Yan, Y.; Mitzi, D. B. Thin-Film Preparation and S. R.; Hu, J.; Wang, H.; Zwanziger, J. W.; Chabinyc, M. L.; Seshadri, R. 2019 Semiconductor or Metal? High Electrical Conductivity and Strong Semiconductor. Photovoltaics. (A = K, Rb, Cs) Related to Perovskite: Aiding the Rational Design of single crystals.

ACS Materials Letters www.acsmaterialsletters.org

Chem. Commun. Halide Perovskite Semiconductors. Trihalide Perovskite Absorber. M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J. Electron Jones, S. C.; De Angelis, F.; Zhu, X. Y. Large polarons in lead halide M. A.; Snaith, H. J.; Giustino, F.; Johnston, M. B.; Herz, L. M. Charge-Carrier Dynamics in 2D Hybrid Metal quantum efficiency.

Perspective

ACS Materials Lett. 2020, 2, 1218−1232
(79) Benin, B. M.; McCall, K. M.; Woerle, M.; Morad, V.; Aebl, M.; Yakunin, S.; Shynkarenko, Y.; Kovalenko, M. V. The Rh-Bi3−,SnBr6Cl16 family: A Fully Inorganic Solid Solution with Room-Temperature Luminescent Members. Angew. Chem., Int. Ed. 2020, 59, 14490−14497.

(80) Krebs, B.; Büscher, K. Dimere Halogenotellurate (IV): Darstellung und Kristallstruktur von [(C6H5)3P]2TeBr10. Z. Anorg. Allg. Chem. 1980, 463, 56−64.

(81) Wang, S.; Mitzi, D. B.; Feild, C. A.; Guloy, A. Synthesis and Characterization of [NH4][Cu(II)−NH3]2MIL (M = Sn, Pb): Stereochemical Activity in Divalent Tin and Lead Halides Containing Single (110) Perovskite Sheets. J. Am. Chem. Soc. 1995, 117, 5297−5302.

(82) Kisajdzya, M.; Gagor, A.; Piesza-Biseroick, A.; Ciàman, A.; Medycyki, W.; Jakubas, R. Exploring a hybrid ferroelectric with a 1-D perovskite-like structure: bis(pyrrolidinium) pentachlorotellurate(III). J. Mater. Chem. C 2019, 7, 10360−10370.

(83) Krebs, B.; Buss, B.; Berger, W. Kristall- und Moleküllstruktur von TeC14PCL5 (=PCL4TeC14). Der stereochemische Einfluß des inerten Elektronenaustauschs in Tellur(IV)-chlorverbindungen. Z. Anorg. Allg. Chem. 1973, 397, 1−15.

(84) Piecha, A.; Pietrzaszko, A.; Bator, G.; Jakubas, R. Structural characterization and ferroelectric ordering in (C6H5)3PBr11. J. Solid State Chem. 2008, 181, 1155−1166.

(85) Wang, Z.; Zhang, Z.; Tao, L.; Shen, N.; Hu, B.; Gong, L.; Li, J.; Chen, X.; Huang, X-Y. Hybrid Chloroantimonates(III): Thermally and Formamidinium Lead Bromide. Inorg. Chem. 2015, 54, 7322−7329.

(86) Blasse, G.; Dirksen, G. J.; Abriel, W. The influence of distortion of the Te(IV) coordination octahedron on its luminescence. Chem. Phys. Lett. 1987, 136, 460−464.

(87) Krebs, B.; Ahlers, F.-P. Developments in Chalcogen−Halide Chemistry. Adv. Inorg. Chem. 1990, 35, 235−317.

(88) Stufkens, D. J. Dynamic Jahn−Teller effect in the excited states of SeC142−, SeBr62−, TeC142− and TeBr62−: Interpretation of electronic absorption and Raman spectra. Recl. Trav. Chim. Pays-Bas 1970, 89, 1185−1201.

(89) Chen, X.; Huang, X.-Y. Hybrid Chloroantimonates(III): Thermally inactive lone pair electrons in some six-coordinate, group 15 halides. Inorg. Chem. 2017, 90, 1711−1775.

(90) Shannon, R. Revised effective ionic radii and radii of interatomic distances in halides and chalcogenides. Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. 1976, 32, 751−767.

(91) Degen, J.; Schmidtke, H. H.; Chatzidimitriou-Dreismann, C. A.; Baser, K. Dimere Halogenotellurate(IV): Stereochemically active or inactive lone pair electrons in some six-coordinate, group 15 halides. J. Am. Chem. Soc. 1992, 114, 4776−4784.

(92) Morss, L. R.; Siegel, M.; Stenger, L.; Edelstein, N. Preparation of cubic chloro complex compounds of trivalent metals: Cs2NaMCl6. Inorg. Chem. 1970, 9, 1771−1775.

(93) Chen, D.; Dai, F.; Hao, S.; Zhou, G.; Liu, Q.; Wolverton, C. M.; Wang, Z. M. M.; Xiao, Z.; Wu, C. Z.; Yang, G.; Chen, S.; Deng, L. Z.; Yu, Q. K.; Feng, G. Y.; Wang, J.; M. B. Revealing the Origin of Luminescence Center in 0D Cs3PbBr6 Perovskite. Chem. Mater. 2019, 31, 9098−9104.

(94) Xu, J.; Li, S.; Qin, C.; Feng, Z.; Du, Y. Identification of Singlet Self-Trapped Excitons in a New Family of White-Light-Emitting Zero-Dimensional Compounds. J. Phys. Chem. C 2020, 124, 11625−11630.

(95) Jing, Y.; Liu, Y.; Jiang, X.; Molokeev, M. S.; Lin, Z.; Xia, Z.; Bopant and Halogen Substitution Triggered Highly Efficient and Tunable Emission in Lead-Free Metal Halide Single Crystals. Chem. Mater. 2020, 32, 5327−5334.

(96) Blasse, G.; Grabmaier, B. C. Luminescent Materials; Springer: Berlin, 1994.

(97) Jacobs, P. W. M. Alkali halide crystals containing impurity ions with the ns2 ground-state electronic configuration. J. Phys. Chem. Solids 1991, 52, 35−67.

(98) Pelant, I.; Valenta, J. Luminescence Spectroscopy of Semiconductors; Oxford University Press: New York, 2012.

(99) Luo, J.; Wang, X.; Li, S.; Liu, J.; Guo, Y.; Niu, G.; Yao, L.; Fu, Y.; Gao, L.; Dong, Q.; Zhao, C.; Leng, M.; Ma, F.; Liang, W.; Wang, L.; Jin, S.; Han, J.; Zhang, L.; Etheridge, J.; Wang, J.; Yan, Y.; Sargent, E. H.; Tang, J. Efficient and stable emission of warm-white light from lead-free halide double perovskites. Nature 2018, 563, 541−545.

(100) Li, S.; Luo, J.; Liu, J.; Tang, J. Self-Trapped Excitons in All-Inorganic Halide Perovskites: Fundamentals, Status, and Potential Applications. J. Phys. Chem. Lett. 2019, 10, 1999−2007.

(101) Sedakova, T. V.; Mirochnik, A. G.; Karasev, V. E. Structure and luminescence properties of tellurium(IV) complex compounds. Opt. Spectrosc. 2011, 110, 755.

(102) Sedakova, T. V.; Mirochnik, A. G. Luminescent and thermochromic properties oftellurium(IV) halide complexes with cesium. Opt. Spectrosc. 2016, 120, 268−273.

(103) Dotsenko, A. A.; Vovna, V. I.; Korochents, V. V.; Mirochnik, A. G.; Shcheka, O. L.; Sedakova, T. V.; Sergienko, V. I. Halide Perovskite-Derived Compounds Rb2TeX6 (X = Cs, Br, and I): Electronic Structure of the Ground and First Excited States. Inorg. Chem. 2019, 58, 6796−6803.

(104) Li, J.; Stoumpos, C. C.; Trimarchi, G. G.; Chung, I.; Mao, L.; Chen, M.; Wasielewski, M. R.; Wang, L.; Kanatzidis, M. G. Air-Stable Direct Bandgap Perovskite Semiconductors: All-Inorganic Tin-Based Heteroleptic Halides A SnCl3+ (A = Cs, Rb). Chem. Mater. 2018, 30, 4847−4856.
(117) Donaldson, J. D.; Grimes, S. M. The inorganic chemistry of tin. In Chemistry of Tin; Smith, P. J., Ed.; Springer: Dordrecht, The Netherlands, 1998; pp 62–94.

(118) Morad, V.; Yakunin, S.; Kovalenko, M. V. Supramolecular Approach for Fine-Tuning of the Bright Luminescence from Zero-Dimensional Antimony(III) Halides. ACS Mater. Lett. 2020, 2, 845–852.

(119) He, Q.; Zhou, C.; Xu, L.; Lee, S.; Lin, X.; Neuj, J.; Worku, M.; Chaaban, M.; Ma, B. Highly Stable Organic Antimony Halide Crystals for X-ray Scinitillation. ACS Mater. Lett. 2020, 2, 633–638.

(120) Fu, P.; Huang, M.; Shang, Y.; Yu, N.; Zhou, H.-L.; Zhang, Y.-B.; Chen, S.; Gong, J.; Ning, Z. Organic–Inorganic Layered and Hollow Tin Bromide Perovskite with Tstile Broadband Emission. ACS Appl. Mater. Interfaces 2018, 10, 34363–34369.

(121) Xu, L.-J.; Lin, H.; Lee, S.; Zhou, C.; Worku, M.; Chaaban, M.; He, Q.; Plavnik, A.; Lin, X.; Chen, B.; Du, M.-H.; Ma, B. 0D Electronic Structure. Hu, Q.; Yin, L.; Xue, K.-H.; Lifshitz, E.; Miao, X.; Tang, J. All-Inorganic Phys. Chem. Lett. 2020, 11, 199–205.

(122) Zhou, C.; Worku, M.; Neuj, J.; Lin, H.; Tian, Y.; Lee, S.; Zhou, Y.; Han, D.; Chen, S.; Hao, A.; Djurovich, P.; Siegrist, T.; Du, M.-H.; Ma, B. Facile Preparation of Light Emitting Organic Metal Halide Crystals with Near-Unity Quantum Efficiency. Chem. Mater. 2018, 30, 2374–2378.

(123) Chabot, B.; Parthe, E. Cs$_2$SB$_2$I$_7$ and Cs$_2$Bi$_2$I$_7$ with the hexagonal C$_6$h$_2$C$_6$h$_1$ structure type. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1978, 34, 646–648.

(124) Zhou, C.; Lin, H.; Neuj, J.; Zhou, Y.; Chaaban, M.; Lee, S.; Worku, M.; Chen, B.; Clark, R.; Cheng, W.; Guan, J.; Djurovich, P.; Zhang, D.; Liu, X.; Bullock, J.; Pak, C.; Shtruk, M.; Du, M.-H.; Siegrist, T.; Ma, B. Green Emitting Single–Crystalline Bulk Assembly of Metal Halide Clusters with Near-Unity Photoluminescence Quantum Efficiency. ACS Energy Lett. 2019, 4, 1579–1583.

(125) Ueta, M.; Kanzaki, H.; Kobayashi, K.; Toyozawa, Y.; Hanamura, E. Exciton–Phonon Processes in Silver Halides. In Excitonic Processes in Solids; Ueta, M., Kanzaki, H., Kobayashi, K., Toyozawa, Y., Hanamura, E., Eds.; Springer: Berlin, 1986; pp 309–369.

(126) Song, K. S.; Williams, R. T. Silver Halide Photodetectors. In Inorganic Layered and Hollow Oxides: Structures, and Optical Properties of (CH$_3$NH$_3$)$_2$CdX$_4$ (X = Cl, Br, I). ACC Mater. Lett. 2020, 2, 1218–1232.