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Why are Double Perovskite Iodides so Rare?

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ABSTRACT. Following on the heels of the remarkable lead halide perovskite optoelectronic materials, interest in lead-free halide perovskites has grown rapidly in the past decade. Double perovskite halides with the general formula $A_2M^IM^{III}X_6$ (where A is a large monovalent cation in the perovskite A site, M^I is a univalent metal, M^{III} is a trivalent metal, and X = halide) represent one of the promising classes of such materials and, of these, the iodides are particularly interesting since their band gaps are expected to be similar to those found in the iconic lead-containing phases, $APbI_3$. However, the successful synthesis of $A_2M^IM^{III}I_6$ iodides appears to have been elusive. In this work, we examine the likelihood that double perovskite halides will form, using a combination of the Goldschmidt tolerance factor and the radius ratio of the trivalent metals, M^{III} , and rationalize the rarity of double perovskite iodides in terms of these descriptors. Using this model as the formability criterion, we predict the possible existence of more than 300 hitherto unknown double perovskite iodides with organic and inorganic cations in the A site.

INTRODUCTION

Hybrid lead halide perovskites such as MAPbI₃ (MA = methylammonium, CH₃NH₃) and their inorganic analogues have been widely studied during the past decade due to their remarkable performance as active layers in photovoltaic (PV) cells.^{1,2} However, concerns about the toxicity and stability of the lead-containing materials have stimulated a great deal of interest in the discovery of non-toxic and stable perovskites that might be equally as effective as the parent lead halides.³⁻⁶ One of the strategies for achieving this has been to synthesize double perovskites, also known as elpasolites, [**Figure 1(a)**] of general formula A₂M^IM^{III}X₆ (where A is a monovalent cation on the perovskite A site, M^I and M^{III} are univalent and trivalent metals at the M site, and X is a halide anion), including hybrid and inorganic examples such as (MA)₂AgBiBr₆⁷ and Cs₂AgBiBr₆.³ The band structures of these double perovskites are broadly similar to those of the lead halide perovskites owing to the fact that the trivalent metal often have fully occupied, 6s² shells similar to Pb(II). So far, however, mainly chlorides and bromides have been realized, and their indirect and wide band gaps have limited their efficacy for PV applications. In addition, there has also been extensive work on fluorides, but for other types of applications. Iodide double perovskites are highly desirable since their band gaps are expected to be similar to those found in the parent lead iodides, but the synthesis of iodides appears to have been a challenge. Kinetically stabilized colloidal nanocrystals of Cs₂AgBiI₆ have been obtained by post-synthetic modification of the corresponding chloride and bromide,⁸ and there have been reports of the inorganic Cs₂NaBiI₆ double perovskite,⁹ and the hybrids (MA)₂AgSbI₆¹⁰ and (MA)₂AgBiI₆.¹¹ However, these have not been substantiated by definitive structural characterization and they are not in the usual structure databases. One of the reasons behind the absence of double perovskite iodides is that low-dimensional 3:2:9 phases, such as A₃Bi₂I₉ and A₃Sb₂I₉, usually form in preference to the perovskites

$A_2M^II M^{III}I_6$.^{9,12} Another outcome of attempts to make the 3D double perovskites is the formation of a low-dimensional, face-sharing chain structure with the same chemical composition as the double perovskites (**Figure 1(b)**).¹³ The present study evaluates the formation of both hybrid and inorganic 3D perovskites and makes predictions as to which iodide candidates might be viable as double perovskites.

Figure 1. (a) X-ray structure of $(MA)_2AgBiBr_6$ showing 3D connectivity of alternating $AgBr_6$ and $BiBr_6$ polyhedra with disordered MA cation on the A site.⁷ (b) X-ray structure of $(MA)_2AgRuBr_6$ showing 1D connectivity of alternating $AgBr_6$ and $RuBr_6$ polyhedra.¹³ The insets of (a) and (b) show the ball and stick models of the corner-sharing and face-sharing connectivity in $(MA)_2AgBiBr_6$ and $(MA)_2AgRuBr_6$, respectively.

METHODS

The Goldschmidt tolerance factor (TF)¹⁴ and the octahedral ratio (μ),¹⁵ also known as the radius ratio, have been popular descriptors for engineering halide perovskites. They are defined as follows:

$$TF = \frac{r_A + r_X}{\sqrt{2}[\{r_M(I) + r_M(III)\}/2 + r_X]} \quad (1)$$

$$\mu = \frac{rM(III)}{rX} \quad (2)$$

where rA is the A cation radius, rX is the X anion radius, $rM(I)$ is the $M(I)$ metal radius, and $rM(III)$ is the $M(III)$ metal radius, using the radii of Shannon.^{16,17} The optimal value for the TF is between 0.80 and 1.00, and the μ is required to be ≥ 0.41 or more precisely, $\geq \sqrt{2} - 1$, for the 3D ABX_3 perovskite structure to be stable.¹⁵ Often, the TF alone is sufficient to describe the formability of single metal Pb(II) and Sn(II) perovskites with a variety of A site cations and X halides since the μ is usually ≥ 0.41 for their chlorides, bromides or iodides,¹⁸ The combined application of these two descriptors has recently been extended to inorganic halide double perovskites with the introduction of a third parameter, the octahedral mismatch between the M^I and M^{III} metals.¹⁹ However, we found that these three descriptors cannot distinguish 1D and 3D hybrid halide double perovskites with the same formula $(MA)_2M^IM^{III}X_6$, as in the present work, limiting their applicability in this class of materials.¹²

We have considered all double perovskite halides, both hybrid and inorganic, with known crystal structures either in the Inorganic Crystal Structure Database (ICSD), the Cambridge Crystallographic Data Centre (CCDC) database or in the Crystallography Open Database (COD). Effective ionic radii of the A site cations, M site metals and the halide anions have been utilized for the calculations. For the organic A site cations [e.g. methylammonium (MA) or formamidinium (FA)] the radii were obtained from Kieslich *et al.*,²⁰ and the radii of the inorganic A site cations, M site cations, and X halides were taken from Shannon.¹⁷ We chose the high spin radii for the calculations where both high and low spin radii are available (such as in the cases of certain 3d metals). The tolerance factors were calculated using equation (1), and we considered the ionic radii of the trivalent metals for the calculation of octahedral factors using equation (2).

RESULTS AND DISCUSSION

The use of the dual descriptors has not been reported to have been applied to the case of hybrid double perovskites, such as $(\text{MA})_2\text{M}^{\text{I}}\text{M}^{\text{III}}\text{X}_6$. We have found that these hybrid perovskites form the face-sharing 1D or the corner-sharing 3D structures, depending on the values of the two descriptors [Figure 2(a) and Table 1; see Table S1 in Supporting Information for the values of TF and μ]. The tolerance factors and octahedral ratios of the five known 3D compounds are well within the desired ranges for the corner-connected perovskite structure, but the six known Ru(III) halide phases and one of the In(III) halides adopt the face-shared 1D structures. We attribute the formation of the 1D structure to the fact that the octahedral factors, μ , for the trivalent metals are all less than 0.41 (and in some cases, the tolerance factors are greater than 1.0). Thus, one of the design strategies based on the TF and μ for a hybrid double perovskite with fluoride (radius 1.33 Å), chloride (radius 1.81 Å), bromide (radius 1.96 Å) or iodide (radius 2.2 Å) is that the radii of their trivalent metals (M^{III}) need to be greater than 0.55 Å, 0.74 Å, 0.80 Å or 0.90 Å, respectively, in order to ensure that the octahedral factor exceeds 0.41. Because the radii of trivalent metals tend to be quite small, this condition is much easier to meet with fluorides than with chlorides and bromides, and it is particularly challenging in the cases of iodides. The striking distribution of the known inorganic and hybrid double perovskite structures reflects this reality (Figure 3). Returning to the cases of $(\text{MA})_2\text{AgSbI}_6$ ¹⁰ and $(\text{MA})_2\text{AgBiI}_6$,¹¹ which were claimed to adopt the 3D double perovskite structure, it seems unlikely that the antimony phase is 3D because the tolerance factor and octahedral ratio are well outside the range for this structure type. The hybrid bismuth phase, however, is within the 3D range [see Figure 2(a)]. We note again, however, that both these systems are excellent candidates for crystallizing as the competing 3:2:9 phases.

Figure 2. (a) Tolerance factor versus radius ratio plot for hybrid double perovskite halides; the filled circles (blue) and filled squares (red) represent the face-sharing chain structures and corner-sharing 3D structures, respectively, and the open triangles (black) correspond to the structurally uncharacterized compounds, $(MA)_2AgM^{III}I_6$ ($M = Sb$ and Bi). (b) Tolerance factor versus radius ratio plot for all-inorganic double perovskite halides; the open triangles (blue), open circles (magenta), open squares (black) represent the corner-sharing 3D structures of $A_2M^IM^{III}F_6$, $A_2M^IM^{III}Cl_6$ and $A_2M^IM^{III}Br_6$, respectively, and the filled triangles (blue) and filled circles (magenta) represent the low dimensional Ba_2NiTeO_6 -type or $BaNiO_3$ -type structures of $A_2M^IM^{III}F_6$ and $A_2M^IM^{III}Cl_6$, respectively.

Figure 3. Bar diagram showing the distribution of 3D double perovskite halides with respect to their halide anions. Only the corner-connected 3D structures available on ICSD, CCDC or COD are included.

Concerning the known inorganic $A_2M^I M^{III} X_6$ systems, they virtually all show TF s and μ factors within the desired ranges for adopting the 3D double perovskite structure [Figure 2(b), Table 1 and Table S1, Supporting Information]. Among 161 structurally known compounds with the $A_2M^I M^{III} X_6$ composition (Table 1), 140 crystallize in the corner-sharing 3D structure, of which 126 compounds fulfill the criteria of both the tolerance factor and the octahedral factor, giving rise to 90 % accuracy of our model. 13 compounds fulfill just one of the two criteria, and 1 compound does not fulfill any criterion. It is not clear why Cs_2NaVCl_6 , $Cs_2NaFeCl_6$, $Cs_2AgFeCl_6$ ($\mu = 0.35$) and $Cs_2AgSbBr_6$ ($\mu = 0.37$) form the 3D structure, despite their very low octahedral factors. We are not surprised to find the aluminum fluorides, $A_2M^I AlF_6$ ($A = K, Na, Rb, NH_4$; $M = K, Na, Li, NH_4$), and the copper fluorides, $A_2M^I CuF_6$ ($A = K, Cs$; $M = Na, K$), in the 3D regime since their octahedral factors are only marginally less than 0.41 and the TF s are well within the perovskite range. Besides these 3D compounds, a few inorganic compounds are known with chemical

formulae analogous to the double perovskites, $\mu > 0.41$ and TF s greater than one. The A site cations in these compounds are too large to form the perovskite structure, so they crystallize in low dimensional hexagonal structures.²⁰ With the exception of the face-sharing chain compound, $\text{Cs}_2\text{LiGaF}_6$, these low-dimensional compounds adopt the $\text{Ba}_2\text{NiTeO}_6$ -type structure. The $\text{Ba}_2\text{NiTeO}_6$ -type structure contains both corner- and face-sharing octahedra, and lies between the corner-sharing 3D structure and the face-sharing 1D structure. These are designated as 1D-3D in the Table 1. The different structural behavior of $\text{Cs}_2\text{LiGaF}_6$ could be attributed to its very high TF of 1.12. It is worthwhile mentioning that the rarity of 1D chain type inorganic $A_2M^I M^{III} X_6$ systems provides an opportunity for seeking new phases with larger A site cations (though there are hybrid and inorganic examples of the 1D ABX_3 chain structure with single M metals, as in the cases of $(\text{C}_3\text{H}_4\text{NS})\text{CdBr}_3$ ²¹ and RbFeBr_3 ²²). Although $\text{Cs}_2\text{AgCrCl}_6$ has a TF within the range for a perovskite structure, it adopts the $\text{Ba}_2\text{NiTeO}_6$ -type structure due to its low octahedral factor. We draw attention to the case of $\text{Cs}_2\text{LiInCl}_6$, which, in spite of its suitable TF and μ factor, adopts the $\text{Ba}_2\text{NiTeO}_6$ -type structure.

Table 1. Structurally characterized hybrid (shaded) and inorganic (unshaded) double perovskites and perovskite related compounds, and their dimensionalities. Structures reported at room temperature and atmospheric pressure in the ICSD, CCDC and COD are taken into consideration.

Compounds (Dim.)	Ref.	Compounds (Dim.)	Ref.	Compounds (Dim.)	Ref.
$(\text{MA})_2\text{NaRuCl}_6$ (1D)	¹³	$\text{Na}_2\text{NaGdBr}_6$ (3D)	²³	$\text{Rb}_2\text{NaCrF}_6$ (3D)	²⁴
$(\text{MA})_2\text{KRuCl}_6$ (1D)	¹³	K_2NaScF_6 (3D)	²⁵	Rb_2KCrF_6 (3D)	²⁴
$(\text{MA})_2\text{AgRuCl}_6$ (1D)	¹³	$\text{Cs}_2\text{NaScF}_6$ (3D)	²⁶	$\text{Na}_2\text{NaCrF}_6$ (3D)	²⁷

(MA) ₂ NaRuBr ₆ (1D)	13	Rb ₂ KScF ₆ (3D)	a	(NH ₄) ₂ NaCrF ₆ (3D)	28
(MA) ₂ KRuBr ₆ (1D)	13	(NH ₄) ₂ NH ₄ ScF ₆ (3D)	29	Cs ₂ KMnF ₆ (3D)	30
(MA) ₂ AgRuBr ₆ (1D)	13	Na ₂ NaScF ₆ (3D)	31	Rb ₂ NaMnF ₆ (3D)	24
(MA) ₂ AgInBr ₆ (1D)	32	Rb ₂ KTiF ₆ (3D)	33	K ₂ NaMnF ₆ (3D)	34
(MA) ₂ KGdCl ₆ (3D)	35	Rb ₂ NaTiF ₆ (3D)	36	Na ₂ NaMnF ₆ (3D)	37
(MA) ₂ KYCl ₆ (3D)	35	Cs ₂ KTiF ₆ (3D)	36	Cs ₂ TiFeF ₆ (3D)	38
(MA) ₂ KBiCl ₆ (3D)	39	Tl ₂ TiTiF ₆ (3D)	36	Cs ₂ KFeF ₆ (3D)	38
(MA) ₂ AgBiBr ₆ (3D)	7	(NH ₄) ₂ NH ₄ TiF ₆ (3D)	a	Rb ₂ KFeF ₆ (3D)	38
(MA) ₂ TlBiBr ₆ (3D)	40	K ₂ NaAlF ₆ (3D)	41	Rb ₂ NaFeF ₆ (3D)	38
Cs ₂ KScCl ₆ (3D)	42	Na ₂ LiAlF ₆ (3D)	43	K ₂ NaFeF ₆ (3D)	44
Cs ₂ CsScCl ₆ (3D)	45	Rb ₂ NaAlF ₆ (3D)	46	(NH ₄) ₂ NaFeF ₆ (3D)	28
Rb ₂ RbScCl ₆ (3D)	45	Na ₂ NaAlF ₆ (3D)	47	(NH ₄) ₂ NH ₄ FeF ₆ (3D)	48
Na ₂ NaScCl ₆ (3D)	49	(NH ₄) ₂ NaAlF ₆ (3D)	50	Cs ₂ KCoF ₆ (3D)	51
Cs ₂ NaVCl ₆ (3D)	52	(NH ₄) ₂ NH ₄ AlF ₆ (3D)	53	Rb ₂ KCoF ₆ (3D)	51
Cs ₂ NaFeCl ₆ (3D)	54	K ₂ NaYF ₆ (3D)	30	Rb ₂ NaCoF ₆ (3D)	51
Cs ₂ AgFeCl ₆ (3D)	55	Rb ₂ NaYF ₆ (3D)	a	Cs ₂ KNiF ₆ (3D)	56
Cs ₂ AgBiCl ₆ (3D)	57	Rb ₂ KYF ₆ (3D)	a	Na ₂ NaNiF ₆ (3D)	58
Cs ₂ NaBiCl ₆ (3D)	59	K ₂ KYF ₆ (3D)	60	Rb ₂ NaNiF ₆ (3D)	56
Cs ₂ AgSbCl ₆ (3D)	61	Cs ₂ NaYF ₆ (3D)	a	Rb ₂ KNiF ₆ (3D)	56
Cs ₂ AgInCl ₆ (3D)	62	Cs ₂ KYF ₆ (3D)	63	K ₂ NaNiF ₆ (3D)	56
Cs ₂ NaInCl ₆ (3D)	64	Cs ₂ RbYF ₆ (3D)	a	Cs ₂ KCuF ₆ (3D)	65
Cs ₂ AgTiCl ₆ (3D)	66	Rb ₂ NaHoF ₆ (3D)	67	K ₂ NaCuF ₆ (3D)	30

Cs ₂ NaLaCl ₆ (3D)	68	Cs ₂ KHoF ₆ (3D)	69	Cs ₂ KMoF ₆ (3D)	70
Cs ₂ NaBkCl ₆ (3D)	71	Cs ₂ RbDyF ₆ (3D)	69	Cs ₂ TlMoF ₆ (3D)	70
Cs ₂ NaYCl ₆ (3D)	25	Rb ₂ NaErF ₆ (3D)	72	Rb ₂ KMoF ₆ (3D)	70
Cs ₂ LiYCl ₆ (3D)	25	Cs ₂ NaErF ₆ (3D)	72	Rb ₂ NaMoF ₆ (3D)	70
Na ₂ NaYCl ₆ (3D)	73	Rb ₂ KInF ₆ (3D)	74	Tl ₂ KMoF ₆ (3D)	70
Cs ₂ NaCeCl ₆ (3D)	75	K ₂ NaInF ₆ (3D)	30	Tl ₂ NaMoF ₆ (3D)	70
Cs ₂ NaSmCl ₆ (3D)	a	Cs ₂ NaInF ₆ (3D)	76	K ₂ NaMoF ₆ (3D)	70
Cs ₂ KSmCl ₆ (3D)	a	(NH ₄) ₂ NaInF ₆ (3D)	77	K ₂ KMoF ₆ (3D)	78
Cs ₂ KEuCl ₆ (3D)	79	Cs ₂ NaBiF ₆ (3D)	a	Cs ₂ KRhF ₆ (3D)	80
Cs ₂ KTbCl ₆ (3D)	79	Cs ₂ KBiF ₆ (3D)	a	Rb ₂ KRhF ₆ (3D)	80
Cs ₂ NaTbCl ₆ (3D)	81	Cs ₂ RbBiF ₆ (3D)	a	Tl ₂ NaRhF ₆ (3D)	80
Na ₂ NaDyCl ₆ (3D)	82	Cs ₂ TlBiF ₆ (3D)	a	Rb ₂ NaRhF ₆ (3D)	80
Cs ₂ NaHoCl ₆ (3D)	83	Rb ₂ NaBiF ₆ (3D)	a	K ₂ NaRhF ₆ (3D)	80
Na ₂ NaHoCl ₆ (3D)	84	Rb ₂ KBiF ₆ (3D)	a	Cs ₂ KAgF ₆ (3D)	85
Cs ₂ NaErCl ₆ (3D)	a	Rb ₂ KGaF ₆ (3D)	86	Cs ₂ LiScCl ₆ (1D-3D)	25
Na ₂ NaErCl ₆ (3D)	87	(NH ₄) ₂ NaGaF ₆ (3D)	28	Cs ₂ LiInCl ₆ (1D-3D)	25
Rb ₂ NaTmCl ₆ (3D)	a	K ₂ NaTlF ₆ (3D)	30	Cs ₂ AgCrCl ₆ (1D-3D)	88
Cs ₂ NaYbCl ₆ (3D)	a	Cs ₂ NaTlF ₆ (3D)	30	Rb ₂ LiGaF ₆ (1D-3D)	89
Cs ₂ LiLuCl ₆ (3D)	42	Cs ₂ TlTlF ₆ (3D)	90	Cs ₂ LiGaF ₆ (1D)	91
Cs ₂ NaUCl ₆ (3D)	92	Cs ₂ TlVF ₆ (3D)	93	Cs ₂ NaCrF ₆ (1D-3D)	91
Cs ₂ TlTiCl ₆ (3D)	90	Cs ₂ KVF ₆ (3D)	93	Cs ₂ NaMnF ₆ (1D-3D)	94
Cs ₂ AgAuCl ₆ (3D)	95	Rb ₂ KVF ₆ (3D)	93	Cs ₂ NaCoF ₆ (1D-3D)	51

$\text{Na}_2\text{NaTiCl}_6$ (3D)	⁹⁶	Rb_2NaVF_6 (3D)	⁹³	$\text{Rb}_2\text{LiFeF}_6$ (1D-3D)	⁹⁷
$\text{Cs}_2\text{AgBiBr}_6$ (3D)	³	K_2NaVF_6 (3D)	^a	$\text{Cs}_2\text{NaFeF}_6$ (1D-3D)	⁹⁷
$\text{Cs}_2\text{AgTlBr}_6$ (3D)	⁶⁶	Na_2NaVF_6 (3D)	⁹⁸	$\text{Cs}_2\text{NaNiF}_6$ (1D-3D)	⁵⁶
$\text{Cs}_2\text{AgSbBr}_6$ (3D)	⁹⁹	$(\text{NH}_4)_2\text{NaVF}_6$ (3D)	⁹⁸	$\text{Cs}_2\text{NaTiF}_6$ (1D-3D)	³⁶
$\text{Cs}_2\text{NaYBr}_6$ (3D)	²⁵	$(\text{NH}_4)_2\text{NH}_4\text{VF}_6$ (3D)	^a	$\text{Cs}_2\text{NaAlF}_6$ (1D-3D)	¹⁰⁰
$\text{Na}_2\text{NaYBr}_6$ (3D)	²³	K_2NaCrF_6 (3D)	⁴⁴	K_2LiAlF_6 (1D-3D)	⁹⁷
$\text{Cs}_2\text{NaLaBr}_6$ (3D)	⁶⁸	Cs_2KCrF_6 (3D)	²⁴		

^aData are available in the ICSD, but the respective publications are not available on the web.

The iodide anion, with a large radius of 2.2 Å, can, in principle, form $M^{\text{III}}\text{I}_6$ octahedra in double perovskites as long as the M^{III} cation is large enough. Good candidates are yttrium, bismuth, lanthanides and actinides. By employing both the TF and μ criteria, as described above, we can predict the existence of many hitherto unknown double perovskite iodides, $A_2M^{\text{I}}M^{\text{III}}\text{I}_6$ with K, Rb, Cs, Tl, methylammonium (MA) and formamidinium (FA) as the A site cations, Li, Na, Ag, Tl and K as the M^{I} metals, and Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho and Bi as the M^{III} metals. These are summarized in **Table 2** (see **Table S2** in the Supporting Information for the values of TF and μ). There are also many obvious candidates among the trivalent actinide metals, which we have not included in the list. It is interesting to note that one of these phases, $\text{Cs}_2\text{NaLaI}_6$, has been reported already,^{68,101} but without a full structural characterization so it did not meet our criteria. However, its powder X-ray diffraction pattern was indexed and the authors ascribed it to low symmetry analogues of the cubic double perovskite structure (monoclinic⁶⁸ and orthorhombic¹⁰¹) and the reports appear credible. Similarly, distorted versions of $\text{Cs}_2M^{\text{I}}M^{\text{III}}\text{I}_6$ ($M^{\text{I}} = \text{Li}$ or Na) double

perovskites with slightly smaller ions such as Sc, Ho, Er, Tm and Lu were reported in 1980,¹⁰² but their structures are not available. The list also contains $\text{Cs}_2\text{NaBiI}_6$, as discussed earlier.⁹ There is no reason to assume that all these reports are incorrect and the apparent existence of some iodide examples encourages us to believe that many of our predictions are likely to be valid. Very recently, layered $\text{Cu}_2\text{AgBiI}_6$ has been synthesized and its structure determined. It is stoichiometrically analogous to $\text{Cs}_2\text{AgBiI}_6$, but does not crystallize in the perovskite structure, probably due to its low tolerance factor of only 0.63, even though the radius ratio exceeds 0.41.¹⁰³

Table 2. Predicted double perovskite iodides with corner connected 3D structures.

K_2LiYI_6	K_2AgDyI_6	$\text{Rb}_2\text{TlDyI}_6$	$\text{Tl}_2\text{LiEuI}_6$	$\text{MA}_2\text{NaEuI}_6$
K_2NaYI_6	K_2AgHoI_6	$\text{Rb}_2\text{TlHoI}_6$	$\text{Tl}_2\text{LiGdI}_6$	$\text{MA}_2\text{NaGdI}_6$
K_2KYI_6	K_2KPrI_6	$\text{Cs}_2\text{LiLaI}_6^*$	$\text{Tl}_2\text{LiTbI}_6$	$\text{MA}_2\text{NaTbI}_6$
Rb_2LiYI_6	K_2KNdI_6	$\text{Cs}_2\text{LiCeI}_6$	$\text{Tl}_2\text{LiDyI}_6$	$\text{MA}_2\text{NaDyI}_6$
Rb_2NaYI_6	K_2KPmI_6	$\text{Cs}_2\text{LiPrI}_6$	$\text{Tl}_2\text{LiHoI}_6$	$\text{MA}_2\text{NaHoI}_6$
Rb_2KYI_6	K_2KSmI_6	$\text{Cs}_2\text{LiNdI}_6$	$\text{Tl}_2\text{NaLaI}_6$	$\text{MA}_2\text{AgLaI}_6$
Rb_2TiYI_6	K_2KEuI_6	$\text{Cs}_2\text{LiPmI}_6$	$\text{Tl}_2\text{NaCeI}_6$	$\text{MA}_2\text{AgCeI}_6$
Tl_2LiYI_6	K_2KGdI_6	$\text{Cs}_2\text{LiSmI}_6$	$\text{Tl}_2\text{NaPrI}_6$	$\text{MA}_2\text{AgPrI}_6$
Tl_2NaYI_6	K_2KTbI_6	$\text{Cs}_2\text{LiEuI}_6$	$\text{Tl}_2\text{NaNdI}_6$	$\text{MA}_2\text{AgNdI}_6$
Tl_2KYI_6	K_2KDyI_6	$\text{Cs}_2\text{LiGdI}_6$	$\text{Tl}_2\text{NaPmI}_6$	$\text{MA}_2\text{AgPmI}_6$
Tl_2AgYI_6	K_2KHoI_6	$\text{Cs}_2\text{LiTbI}_6$	$\text{Tl}_2\text{NaSmI}_6$	$\text{MA}_2\text{AgSmI}_6$
Cs_2LiYI_6	$\text{Rb}_2\text{LiLaI}_6$	$\text{Cs}_2\text{LiDyI}_6$	$\text{Tl}_2\text{NaEuI}_6$	$\text{MA}_2\text{AgEuI}_6$
Cs_2NaYI_6	$\text{Rb}_2\text{LiCeI}_6$	$\text{Cs}_2\text{LiHoI}_6^*$	$\text{Tl}_2\text{NaGdI}_6$	$\text{MA}_2\text{AgGdI}_6$

Cs_2KYI_6	$\text{Rb}_2\text{LiPrI}_6$	$\text{Cs}_2\text{NaLaI}_6$	$\text{Tl}_2\text{NaTbI}_6$	$\text{MA}_2\text{AgTbI}_6$
Cs_2TIYI_6	$\text{Rb}_2\text{LiNdI}_6$	$\text{Cs}_2\text{NaCeI}_6$	$\text{Tl}_2\text{NaDyI}_6$	$\text{MA}_2\text{AgDyI}_6$
K_2LiBiI_6	$\text{Rb}_2\text{LiPmI}_6$	$\text{Cs}_2\text{NaPrI}_6$	$\text{Tl}_2\text{NaHoI}_6$	$\text{MA}_2\text{AgHoI}_6$
K_2NaBiI_6	$\text{Rb}_2\text{LiSmI}_6$	$\text{Cs}_2\text{NaNdI}_6$	$\text{Tl}_2\text{AgLaI}_6$	MA_2KLaI_6
K_2AgBiI_6	$\text{Rb}_2\text{LiEuI}_6$	$\text{Cs}_2\text{NaPmI}_6$	$\text{Tl}_2\text{AgCeI}_6$	MA_2KCeI_6
$\text{Rb}_2\text{LiBiI}_6$	$\text{Rb}_2\text{LiGdI}_6$	$\text{Cs}_2\text{NaSmI}_6$	$\text{Tl}_2\text{AgPrI}_6$	MA_2KPrI_6
$\text{Rb}_2\text{NaBiI}_6$	$\text{Rb}_2\text{LiTbI}_6$	$\text{Cs}_2\text{NaEuI}_6$	$\text{Tl}_2\text{AgNdI}_6$	MA_2KNdI_6
$\text{Rb}_2\text{AgBiI}_6$	$\text{Rb}_2\text{LiDyI}_6$	$\text{Cs}_2\text{NaGdI}_6$	$\text{Tl}_2\text{AgPmI}_6$	MA_2KPmI_6
Rb_2KBiI_6	$\text{Rb}_2\text{LiHoI}_6$	$\text{Cs}_2\text{NaTbI}_6$	$\text{Tl}_2\text{AgSmI}_6$	MA_2KSmI_6
$\text{Rb}_2\text{TlBiI}_6$	$\text{Rb}_2\text{NaLaI}_6$	$\text{Cs}_2\text{NaDyI}_6$	$\text{Tl}_2\text{AgEuI}_6$	MA_2KEuI_6
$\text{Tl}_2\text{LiBiI}_6$	$\text{Rb}_2\text{NaCeI}_6$	$\text{Cs}_2\text{NaHoI}_6$	$\text{Tl}_2\text{AgGdI}_6$	MA_2KGdI_6
$\text{Tl}_2\text{NaBiI}_6$	$\text{Rb}_2\text{NaPrI}_6$	$\text{Cs}_2\text{AgLaI}_6$	$\text{Tl}_2\text{AgTbI}_6$	MA_2KTbI_6
$\text{Tl}_2\text{AgBiI}_6$	$\text{Rb}_2\text{NaNdI}_6$	$\text{Cs}_2\text{AgCeI}_6$	$\text{Tl}_2\text{AgDyI}_6$	MA_2KDyI_6
Tl_2KBiI_6	$\text{Rb}_2\text{NaPmI}_6$	$\text{Cs}_2\text{AgPrI}_6$	$\text{Tl}_2\text{AgHoI}_6$	MA_2KHoI_6
$\text{Cs}_2\text{LiBiI}_6$	$\text{Rb}_2\text{NaSmI}_6$	$\text{Cs}_2\text{AgNdI}_6$	Tl_2KLaI_6	$\text{MA}_2\text{TlLaI}_6$
$\text{Cs}_2\text{NaBiI}_6^*$	$\text{Rb}_2\text{NaEuI}_6$	$\text{Cs}_2\text{AgPmI}_6$	Tl_2KCeI_6	$\text{MA}_2\text{TlCeI}_6$
$\text{Cs}_2\text{AgBiI}_6^*$	$\text{Rb}_2\text{NaGdI}_6$	$\text{Cs}_2\text{AgSmI}_6$	Tl_2KPrI_6	$\text{MA}_2\text{TlPrI}_6$
Cs_2KBiI_6	$\text{Rb}_2\text{NaTbI}_6$	$\text{Cs}_2\text{AgEuI}_6$	Tl_2KNdI_6	$\text{MA}_2\text{TlNdI}_6$
$\text{Cs}_2\text{TlBiI}_6$	$\text{Rb}_2\text{NaDyI}_6$	$\text{Cs}_2\text{AgGdI}_6$	Tl_2KPmI_6	$\text{MA}_2\text{TlPmI}_6$
K_2LiLaI_6	$\text{Rb}_2\text{NaHoI}_6$	$\text{Cs}_2\text{AgTbI}_6$	Tl_2KSmI_6	$\text{MA}_2\text{TlSmI}_6$
K_2LiCeI_6	$\text{Rb}_2\text{AgLaI}_6$	$\text{Cs}_2\text{AgDyI}_6$	Tl_2KEuI_6	$\text{MA}_2\text{TlEuI}_6$
K_2LiPrI_6	$\text{Rb}_2\text{AgCeI}_6$	$\text{Cs}_2\text{AgHoI}_6$	Tl_2KGdI_6	$\text{MA}_2\text{TlGdI}_6$

K_2LiNdI_6	Rb_2AgPrI_6	Cs_2KLaI_6	Tl_2KTbI_6	MA_2TiTbI_6
K_2LiPmI_6	Rb_2AgNdI_6	Cs_2KCeI_6	Tl_2KDyI_6	MA_2TiDyI_6
K_2LiSmI_6	Rb_2AgPmI_6	Cs_2KPrI_6	Tl_2KHoI_6	MA_2TiHoI_6
K_2LiEuI_6	Rb_2AgSmI_6	Cs_2KNdI_6	MA_2NaYI_6	FA_2KBiI_6
K_2LiGdI_6	Rb_2AgEuI_6	Cs_2KPmI_6	MA_2KYI_6	FA_2KLaI_6
K_2LiTbI_6	Rb_2AgGdI_6	Cs_2KSmI_6	MA_2TiYI_6	FA_2KCeI_6
K_2LiDyI_6	Rb_2AgTbI_6	Cs_2KEuI_6	MA_2LiBiI_6	FA_2KPrI_6
K_2LiHoI_6	Rb_2AgDyI_6	Cs_2KGdI_6	MA_2NaBiI_6	FA_2KNdI_6
K_2NaLaI_6	Rb_2AgHoI_6	Cs_2KTbI_6	$MA_2AgBiI_6^*$	FA_2KPmI_6
K_2NaCeI_6	Rb_2KLaI_6	Cs_2KDyI_6	MA_2KBiI_6	FA_2KSmI_6
K_2NaPrI_6	Rb_2KCeI_6	Cs_2KHoI_6	MA_2TiBiI_6	FA_2KEuI_6
K_2NaNdI_6	Rb_2KPrI_6	Cs_2TiLaI_6	MA_2LiLaI_6	FA_2KGdI_6
K_2NaPmI_6	Rb_2KNdI_6	Cs_2TiCeI_6	MA_2LiCeI_6	FA_2KTbI_6
K_2NaSmI_6	Rb_2KPmI_6	Cs_2TiPrI_6	MA_2LiPrI_6	FA_2KDyI_6
K_2NaEuI_6	Rb_2KSmI_6	Cs_2TiNdI_6	MA_2LiNdI_6	FA_2KHoI_6
K_2NaGdI_6	Rb_2KEuI_6	Cs_2TiPmI_6	MA_2LiPmI_6	FA_2TiYI_6
K_2NaTbI_6	Rb_2KGdI_6	Cs_2TiSmI_6	MA_2LiSmI_6	FA_2TiLaI_6
K_2NaDyI_6	Rb_2KTbI_6	Cs_2TiEuI_6	MA_2LiEuI_6	FA_2TiCeI_6
K_2NaHoI_6	Rb_2KDyI_6	Cs_2TiGdI_6	MA_2LiGdI_6	FA_2TiPrI_6
K_2AgLaI_6	Rb_2KHoI_6	Cs_2TiTbI_6	MA_2LiTbI_6	FA_2TiNdI_6
K_2AgCeI_6	Rb_2TiCeI_6	Cs_2TiDyI_6	MA_2LiDyI_6	FA_2TiPmI_6
K_2AgPrI_6	Rb_2TiPrI_6	Cs_2TiHoI_6	MA_2LiHoI_6	FA_2TiSmI_6

K_2AgNdI_6	Rb_2TiNdI_6	Tl_2LiLaI_6	MA_2NaLaI_6	FA_2TiEuI_6
K_2AgPmI_6	Rb_2TiPmI_6	Tl_2LiCeI_6	MA_2NaCeI_6	FA_2TiGdI_6
K_2AgSmI_6	Rb_2TiSmI_6	Tl_2LiPrI_6	MA_2NaPrI_6	FA_2TiTbI_6
K_2AgEuI_6	Rb_2TiEuI_6	Tl_2LiNdI_6	MA_2NaNdI_6	FA_2TiDyI_6
K_2AgGdI_6	Rb_2TiGdI_6	Tl_2LiPmI_6	MA_2NaPmI_6	FA_2TiHoI_6
K_2AgTbI_6	Rb_2TiTbI_6	Tl_2LiSmI_6	MA_2NaSmI_6	

*Reported, but without structural characterization.

It is reasonable to ask how more than 300 double perovskite iodides could possibly have eluded discovery when there is so much interest in the area. One factor is certainly the tendency of the Bi(III) compounds to crystallize as low-dimensional 3:2:9 type phases due to their high covalency, with bismuth halide compounds notably favoring layered-type structures.¹⁰⁴ Most of our predictions, however, relate to rare-earth phases, and we believe that the challenges of synthesizing these lanthanide compounds are much greater than those encountered with post-transition metals. In particular, both the starting materials and products are likely to be air-sensitive and require rigorous exclusion of moisture. The case of Cs_2NaErI_6 , for example,¹⁰² involved a solid state reaction between carefully-dried CsI, NaI, Er metal and I_2 in a sealed tantalum tube, rather than a simple reaction in aqueous solution. The rare earth metal iodides are more ionic than their post transition metal analogues and we would expect their band gaps to be wider than, for example, bismuth-containing compounds.¹⁰⁴ They are, therefore, less likely to be useful for PV applications and more suitable for use in areas such as X-ray detection, and magnetic and optical applications. We are confident that efforts along these lines will lead to the discovery of many of the compounds listed in Table 2.

CONCLUSIONS

By combining the Goldschmidt tolerance factor and the radius ratio of the trivalent metal, we developed a model to describe the formability of halide double perovskites. We calculated these two geometrical factors for 161 structurally known compounds of formula $A_2M^IM^{III}X_6$, including 103 fluorides, 45 chlorides and 13 bromides, to validate our approach. Of these, 92 fluorides, 39 chlorides and 9 bromides crystallize in the double perovskite structure and our model describes them with $\sim 90\%$ accuracy. Clearly, their number decreases rapidly on moving down the halogen family ($F \rightarrow Cl \rightarrow Br \rightarrow I$) which we attribute to the fact that, while fluoride can combine with a large number of trivalent metals that meet the radius ratio criterion, the number decreases as the halide size increases; it is particularly challenging in the case of iodide. In addition, there are other challenges of synthesizing iodides which hamper their formation, such as the moisture sensitivity of the rare-earth iodides and the preferential formation of low-dimensional 3:2:9 phases in the case of Bi(III) compounds. Our model also applies to hybrid systems and it clearly distinguishes 1D and 3D hybrid double perovskite halides with the same formula, $(MA)_2M^IM^{III}X_6$. Based on these outcomes, we have generated a list of more than 300 hitherto unknown double perovskite iodides of yttrium, bismuth and the lanthanide metals. The predicted iodides are expected to show interesting optoelectronic and other properties, and we believe this work will stimulate their discovery.

ASSOCIATED CONTENT

Supporting Information. Full tables of existing double perovskite halides and the predicted double perovskite iodides are provided with their tolerance factors and radius ratios. This material is available free of charge at <http://pubs.acs.org>.

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Notes

The authors declare no conflict of interest.

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For Table of Contents Graphic Only

Supporting information for:
Why are Double Perovskite Iodides so Rare?

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Table S1. Structurally characterized hybrid (shaded) and inorganic (unshaded) double perovskites and perovskite related compounds, and their dimensionalities, tolerance factors and radius ratios. The structures reported at room temperature and atmospheric pressure in ICSD, CCDC and COD are taken into consideration.

S. No.	Compounds	Tolerance factor	Radius ratio	Dimensionality
1.	(MA) ₂ NaRuCl ₆	1.058	0.375	1D
2.	(MA) ₂ KRuCl ₆	0.991	0.375	1D
3.	(MA) ₂ AgRuCl ₆	1.033	0.375	1D
4.	(MA) ₂ NaRuBr ₆	1.039	0.347	1D
5.	(MA) ₂ KRuBr ₆	0.976	0.347	1D
6.	(MA) ₂ AgRuBr ₆	1.016	0.346	1D
7.	(MA) ₂ AgInBr ₆	0.995	0.408	1D
8.	(MA) ₂ KBiCl ₆	0.933	0.569	3D
9.	(MA) ₂ KGdCl ₆	0.948	0.518	3D
10.	(MA) ₂ KYCl ₆	0.954	0.497	3D
11.	(MA) ₂ AgBiBr ₆	0.957	0.525	3D
12.	(MA) ₂ TlBiBr ₆	0.905	0.525	3D
13.	Cs ₂ KScCl ₆	0.908	0.411	3D
14.	Cs ₂ CsScCl ₆	0.864	0.411	3D
15.	Rb ₂ RbScCl ₆	0.848	0.411	3D
16.	Na ₂ NaScCl ₆	0.840	0.411	3D
17.	Cs ₂ NaVCl ₆	0.988	0.353	3D
18.	Na ₂ NaTiCl ₆	0.852	0.370	3D
19.	Cs ₂ NaFeCl ₆	0.987	0.356	3D
20.	Cs ₂ AgFeCl ₆	0.963	0.356	3D
21.	Cs ₂ AgBiCl ₆	0.899	0.569	3D
22.	Cs ₂ NaBiCl ₆	0.920	0.569	3D
23.	Cs ₂ AgSbCl ₆	0.943	0.419	3D
24.	Cs ₂ AgInCl ₆	0.937	0.441	3D
25.	Cs ₂ NaInCl ₆	0.959	0.441	3D
26.	Cs ₂ AgTlCl ₆	0.922	0.488	3D
27.	Cs ₂ NaLaCl ₆	0.920	0.569	3D
28.	Cs ₂ NaBkCl ₆	0.932	0.530	3D
29.	Cs ₂ NaYCl ₆	0.942	0.497	3D
30.	Cs ₂ LiYCl ₆	0.988	0.497	3D
31.	Na ₂ NaYCl ₆	0.816	0.497	3D
32.	Cs ₂ NaCeCl ₆	0.923	0.558	3D
33.	Cs ₂ NaSmCl ₆	0.932	0.529	3D
34.	Cs ₂ KSmCl ₆	0.876	0.529	3D
35.	Cs ₂ KEuCl ₆	0.877	0.522	3D
36.	Cs ₂ KTbCl ₆	0.881	0.509	3D

37.	Cs ₂ NaTbCl ₆	0.938	0.509	3D
38.	Na ₂ NaDyCl ₆	0.815	0.503	3D
39.	Cs ₂ NaHoCl ₆	0.941	0.497	3D
40.	Na ₂ NaHoCl ₆	0.816	0.497	3D
41.	Cs ₂ NaErCl ₆	0.943	0.491	3D
42.	Na ₂ NaErCl ₆	0.818	0.491	3D
43.	Rb ₂ NaTmCl ₆	0.904	0.486	3D
44.	Cs ₂ NaYbCl ₆	0.947	0.479	3D
45.	Cs ₂ LiLuCl ₆	0.995	0.475	3D
46.	Cs ₂ NaUCl ₆	0.921	0.566	3D
47.	Cs ₂ TiTiCl ₆	0.869	0.488	3D
48.	Cs ₂ AgAuCl ₆	0.928	0.469	3D
49.	Cs ₂ AgBiBr ₆	0.890	0.525	3D
50.	Cs ₂ AgTlBr ₆	0.912	0.451	3D
51.	Cs ₂ AgSbBr ₆	0.931	0.387	3D
52.	Cs ₂ NaYBr ₆	0.930	0.459	3D
53.	Na ₂ NaYBr ₆	0.811	0.459	3D
54.	Cs ₂ NaLaBr ₆	0.909	0.525	3D
55.	Na ₂ NaGdBr ₆	0.808	0.496	3D
56.	K ₂ NaScF ₆	0.949	0.560	3D
57.	Cs ₂ NaScF ₆	1.026	0.560	3D
58.	Rb ₂ KScF ₆	0.901	0.560	3D
59.	(NH ₄) ₂ NH ₄ ScF ₆	0.868	0.560	3D
60.	Na ₂ NaScF ₆	0.869	0.560	3D
61.	Rb ₂ KTiF ₆	0.915	0.503	3D
62.	Rb ₂ NaTiF ₆	0.991	0.503	3D
63.	Cs ₂ KTiF ₆	0.963	0.503	3D
64.	Tl ₂ TiTiF ₆	0.887	0.503	3D
65.	(NH ₄) ₂ NH ₄ TiF ₆	0.882	0.503	3D
66.	K ₂ NaAlF ₆	0.996	0.402	3D
67.	Na ₂ LiAlF ₆	0.972	0.402	3D
68.	Rb ₂ NaAlF ₆	1.023	0.402	3D
69.	Na ₂ NaAlF ₆	0.912	0.402	3D
70.	(NH ₄) ₂ NaAlF ₆	1.006	0.402	3D
71.	(NH ₄) ₂ NH ₄ AlF ₆	0.907	0.402	3D
72.	K ₂ NaYF ₆	0.917	0.676	3D
73.	Rb ₂ NaYF ₆	0.941	0.676	3D
74.	Rb ₂ KYF ₆	0.873	0.676	3D
75.	K ₂ KYF ₆	0.850	0.676	3D
76.	Cs ₂ NaYF ₆	0.991	0.676	3D
77.	Cs ₂ KYF ₆	0.919	0.676	3D
78.	Cs ₂ RbYF ₆	0.893	0.676	3D
79.	Rb ₂ NaHoF ₆	0.941	0.677	3D

80.	Cs ₂ KHoF ₆	0.918	0.677	3D
81.	Cs ₂ RbDyF ₆	0.891	0.685	3D
82.	Rb ₂ NaErF ₆	0.943	0.669	3D
83.	Cs ₂ NaErF ₆	0.993	0.669	3D
84.	Rb ₂ KInF ₆	0.891	0.601	3D
85.	K ₂ NaInF ₆	0.937	0.601	3D
86.	Cs ₂ NaInF ₆	1.013	0.601	3D
87.	(NH ₄) ₂ NaInF ₆	0.947	0.601	3D
88.	Cs ₂ NaBiF ₆	0.963	0.774	3D
89.	Cs ₂ KBiF ₆	0.895	0.774	3D
90.	Cs ₂ RbBiF ₆	0.871	0.774	3D
91.	Cs ₂ TlBiF ₆	0.874	0.774	3D
92.	Rb ₂ NaBiF ₆	0.915	0.774	3D
93.	Rb ₂ KBiF ₆	0.850	0.774	3D
94.	Rb ₂ KGaF ₆	0.925	0.466	3D
95.	(NH ₄) ₂ NaGaF ₆	0.986	0.466	3D
96.	K ₂ NaTlF ₆	0.920	0.665	3D
97.	Cs ₂ NaTlF ₆	0.994	0.665	3D
98.	Cs ₂ TlTlF ₆	0.899	0.665	3D
99.	Cs ₂ TlVF ₆	0.945	0.481	3D
100.	Cs ₂ KVF ₆	0.970	0.481	3D
101.	Rb ₂ KVF ₆	0.921	0.481	3D
102.	Rb ₂ NaVF ₆	0.998	0.481	3D
103.	K ₂ NaVF ₆	0.972	0.481	3D
104.	Na ₂ NaVF ₆	0.890	0.481	3D
105.	(NH ₄) ₂ NaVF ₆	0.982	0.481	3D
106.	(NH ₄) ₂ NH ₄ VF ₆	0.887	0.481	3D
107.	K ₂ NaCrF ₆	0.978	0.462	3D
108.	Cs ₂ KCrF ₆	0.975	0.462	3D
109.	Rb ₂ NaCrF ₆	1.004	0.462	3D
110.	Rb ₂ KCrF ₆	0.926	0.462	3D
111.	Na ₂ NaCrF ₆	0.895	0.462	3D
112.	(NH ₄) ₂ NaCrF ₆	0.987	0.462	3D
113.	Cs ₂ KMnF ₆	0.969	0.484	3D
114.	Rb ₂ NaMnF ₆	0.997	0.484	3D
115.	K ₂ NaMnF ₆	0.971	0.484	3D
116.	Na ₂ NaMnF ₆	0.889	0.484	3D
117.	Cs ₂ TlFeF ₆	0.944	0.484	3D
118.	Cs ₂ KFeF ₆	0.969	0.484	3D
119.	Rb ₂ KFeF ₆	0.920	0.484	3D
120.	Rb ₂ NaFeF ₆	0.997	0.484	3D
121.	K ₂ NaFeF ₆	0.971	0.484	3D
122.	(NH ₄) ₂ NaFeF ₆	0.981	0.484	3D

123.	(NH ₄) ₂ NH ₄ FeF ₆	0.886	0.484	3D
124.	Cs ₂ KCoF ₆	0.976	0.458	3D
125.	Rb ₂ KCoF ₆	0.927	0.458	3D
126.	Rb ₂ NaCoF ₆	1.005	0.458	3D
127.	Cs ₂ KNiF ₆	0.978	0.451	3D
128.	Na ₂ NaNiF ₆	0.898	0.451	3D
129.	Rb ₂ NaNiF ₆	1.007	0.451	3D
130.	Rb ₂ KNiF ₆	0.929	0.451	3D
131.	K ₂ NaNiF ₆	0.981	0.451	3D
132.	Cs ₂ KCuF ₆	0.991	0.406	3D
133.	K ₂ NaCuF ₆	0.995	0.406	3D
134.	Cs ₂ KMoF ₆	0.959	0.518	3D
135.	Cs ₂ TlMoF ₆	0.936	0.518	3D
136.	Rb ₂ KMoF ₆	0.912	0.518	3D
137.	Rb ₂ NaMoF ₆	0.987	0.518	3D
138.	Tl ₂ KMoF ₆	0.906	0.518	3D
139.	Tl ₂ NaMoF ₆	0.980	0.518	3D
140.	K ₂ NaMoF ₆	0.961	0.518	3D
141.	K ₂ KMoF ₆	0.888	0.518	3D
142.	Cs ₂ KRhF ₆	0.964	0.500	3D
143.	Rb ₂ KRhF ₆	0.916	0.500	3D
144.	Tl ₂ NaRhF ₆	0.986	0.500	3D
145.	Rb ₂ NaRhF ₆	0.992	0.500	3D
146.	K ₂ NaRhF ₆	0.966	0.500	3D
147.	Cs ₂ KAgF ₆	0.947	0.563	3D
148.	Cs ₂ LiScCl ₆	1.018	0.411	Ba ₂ NiTeO ₆ -type
149.	Cs ₂ LiInCl ₆	1.008	0.442	Ba ₂ NiTeO ₆ -type
150.	Cs ₂ AgCrCl ₆	0.969	0.339	Ba ₂ NiTeO ₆ -type
151.	Rb ₂ LiGaF ₆	1.067	0.466	Ba ₂ NiTeO ₆ -type
152.	Cs ₂ LiGaF ₆	1.123	0.466	BaNiO ₃ -type
153.	Cs ₂ NaCrF ₆	1.057	0.462	Ba ₂ NiTeO ₆ -type
154.	Cs ₂ NaMnF ₆	1.049	0.484	Ba ₂ NiTeO ₆ -type
155.	Cs ₂ NaCoF ₆	1.058	0.458	Ba ₂ NiTeO ₆ -type
156.	Rb ₂ LiFeF ₆	1.061	0.484	Ba ₂ NiTeO ₆ -type
157.	Cs ₂ NaFeF ₆	1.049	0.485	Ba ₂ NiTeO ₆ -type
158.	K ₂ LiAlF ₆	1.062	0.402	Ba ₂ NiTeO ₆ -type
159.	Cs ₂ NaAlF ₆	1.077	0.402	Ba ₂ NiTeO ₆ -type
160.	Cs ₂ NaNiF ₆	1.060	0.451	Ba ₂ NiTeO ₆ -type
161.	Cs ₂ NaTiF ₆	1.043	0.503	Ba ₂ NiTeO ₆ -type

Table S2. Predicted double perovskite iodides with corner connected 3D structures, and their tolerance factors and radius ratios.

Sr. No.	Compounds	Tolerance factor	Radius ratio
1.	K ₂ LiYI ₆	0.896	0.409
2.	K ₂ NaYI ₆	0.859	0.409
3.	K ₂ KYI ₆	0.813	0.409
4.	Rb ₂ LiYI ₆	0.915	0.409
5.	Rb ₂ NaYI ₆	0.877	0.409
6.	Rb ₂ KYI ₆	0.830	0.409
7.	Rb ₂ TlYI ₆	0.815	0.409
8.	Tl ₂ LiYI ₆	0.910	0.409
9.	Tl ₂ NaYI ₆	0.872	0.409
10.	Tl ₂ KYI ₆	0.826	0.409
11.	Tl ₂ AgYI ₆	0.855	0.409
12.	Cs ₂ LiYI ₆	0.952	0.409
13.	Cs ₂ NaYI ₆	0.913	0.409
14.	Cs ₂ KYI ₆	0.864	0.409
15.	Cs ₂ TlYI ₆	0.848	0.409
16.	K ₂ LiBiI ₆	0.877	0.468
17.	K ₂ NaBiI ₆	0.842	0.468
18.	K ₂ AgBiI ₆	0.825	0.468
19.	Rb ₂ LiBiI ₆	0.896	0.468
20.	Rb ₂ NaBiI ₆	0.859	0.468
21.	Rb ₂ AgBiI ₆	0.842	0.468
22.	Rb ₂ KBiI ₆	0.814	0.468
23.	Rb ₂ TlBiI ₆	0.800	0.468
24.	Tl ₂ LiBiI ₆	0.891	0.468
25.	Tl ₂ NaBiI ₆	0.855	0.468
26.	Tl ₂ AgBiI ₆	0.838	0.468
27.	Tl ₂ KBiI ₆	0.810	0.468
28.	Cs ₂ LiBiI ₆	0.932	0.468
29.	Cs ₂ NaBiI ₆ *	0.895	0.468
30.	Cs ₂ AgBiI ₆ *	0.877	0.468
31.	Cs ₂ KBiI ₆	0.847	0.468
32.	Cs ₂ TlBiI ₆	0.833	0.468
33.	K ₂ LiLaI ₆	0.877	0.469
34.	K ₂ LiCeI ₆	0.880	0.469
35.	K ₂ LiPrI ₆	0.883	0.450
36.	K ₂ LiNdI ₆	0.884	0.446
37.	K ₂ LiPmI ₆	0.886	0.441
38.	K ₂ LiSmI ₆	0.888	0.435
39.	K ₂ LiEuI ₆	0.889	0.430
40.	K ₂ LiGdI ₆	0.890	0.426
41.	K ₂ LiTbI ₆	0.892	0.419
42.	K ₂ LiDyI ₆	0.894	0.414
43.	K ₂ LiHoI ₆	0.896	0.409
44.	K ₂ NaLaI ₆	0.841	0.469
45.	K ₂ NaCeI ₆	0.844	0.459
46.	K ₂ NaPrI ₆	0.847	0.450

47.	K_2NaNdI_6	0.848	0.446
48.	K_2NaPmI_6	0.850	0.441
49.	K_2NaSmI_6	0.851	0.435
50.	K_2NaEuI_6	0.853	0.430
51.	K_2NaGdI_6	0.854	0.426
52.	K_2NaTbI_6	0.856	0.419
53.	K_2NaDyI_6	0.858	0.414
54.	K_2NaHoI_6	0.859	0.409
55.	K_2AgLaI_6	0.825	0.469
56.	K_2AgCeI_6	0.828	0.459
57.	K_2AgPrI_6	0.830	0.450
58.	K_2AgNdI_6	0.831	0.446
59.	K_2AgPmI_6	0.833	0.441
60.	K_2AgSmI_6	0.834	0.435
61.	K_2AgEuI_6	0.836	0.430
62.	K_2AgGdI_6	0.837	0.426
63.	K_2AgTbI_6	0.839	0.419
64.	K_2AgDyI_6	0.840	0.414
65.	K_2AgHoI_6	0.842	0.409
66.	K_2KPrI_6	0.802	0.450
67.	K_2KNdI_6	0.803	0.446
68.	K_2KPmI_6	0.804	0.441
69.	K_2KSmI_6	0.806	0.435
70.	K_2KEuI_6	0.807	0.430
71.	K_2KGdI_6	0.808	0.426
72.	K_2KTbI_6	0.810	0.419
73.	K_2KDyI_6	0.811	0.414
74.	K_2KHoI_6	0.813	0.409
75.	Rb_2LiLaI_6	0.895	0.469
76.	Rb_2LiCeI_6	0.898	0.459
77.	Rb_2LiPrI_6	0.901	0.450
78.	Rb_2LiNdI_6	0.902	0.446
79.	Rb_2LiPmI_6	0.904	0.441
80.	Rb_2LiSmI_6	0.906	0.435
81.	Rb_2LiEuI_6	0.908	0.430
82.	Rb_2LiGdI_6	0.909	0.426
83.	Rb_2LiTbI_6	0.911	0.419
84.	Rb_2LiDyI_6	0.913	0.414
85.	Rb_2LiHoI_6	0.915	0.409
86.	Rb_2NaLaI_6	0.859	0.469
87.	Rb_2NaCeI_6	0.862	0.459
88.	Rb_2NaPrI_6	0.865	0.450
89.	Rb_2NaNdI_6	0.866	0.446
90.	Rb_2NaPmI_6	0.867	0.441
91.	Rb_2NaSmI_6	0.869	0.435
92.	Rb_2NaEuI_6	0.870	0.430
93.	Rb_2NaGdI_6	0.872	0.426
94.	Rb_2NaTbI_6	0.874	0.419
95.	Rb_2NaDyI_6	0.875	0.414
96.	Rb_2NaHoI_6	0.877	0.409

97.	Rb ₂ AgLaI ₆	0.842	0.469
98.	Rb ₂ AgCeI ₆	0.845	0.459
99.	Rb ₂ AgPrI ₆	0.848	0.450
100.	Rb ₂ AgNdI ₆	0.848	0.446
101.	Rb ₂ AgPmI ₆	0.850	0.440
102.	Rb ₂ AgSmI ₆	0.852	0.435
103.	Rb ₂ AgEuI ₆	0.853	0.430
104.	Rb ₂ AgGdI ₆	0.854	0.426
105.	Rb ₂ AgTbI ₆	0.856	0.419
106.	Rb ₂ AgDyI ₆	0.858	0.414
107.	Rb ₂ AgHoI ₆	0.859	0.409
108.	Rb ₂ KLal ₆	0.814	0.469
109.	Rb ₂ KCeI ₆	0.816	0.459
110.	Rb ₂ KPrI ₆	0.819	0.450
111.	Rb ₂ KNdI ₆	0.819	0.446
112.	Rb ₂ KPmI ₆	0.821	0.440
113.	Rb ₂ KSmI ₆	0.822	0.435
114.	Rb ₂ KEuI ₆	0.824	0.430
115.	Rb ₂ KGdI ₆	0.825	0.426
116.	Rb ₂ KTbI ₆	0.827	0.419
117.	Rb ₂ KDyI ₆	0.828	0.414
118.	Rb ₂ KHoI ₆	0.829	0.409
119.	Rb ₂ TlCeI ₆	0.802	0.459
120.	Rb ₂ TlPrI ₆	0.805	0.450
121.	Rb ₂ TlNdI ₆	0.805	0.446
122.	Rb ₂ TlPmI ₆	0.807	0.440
123.	Rb ₂ TlSmI ₆	0.808	0.435
124.	Rb ₂ TlEuI ₆	0.809	0.430
125.	Rb ₂ TlGdI ₆	0.810	0.426
126.	Rb ₂ TlTbI ₆	0.812	0.419
127.	Rb ₂ TlDyI ₆	0.813	0.414
128.	Rb ₂ TlHoI ₆	0.815	0.409
129.	Cs ₂ LiLaI ₆ *	0.931	0.469
130.	Cs ₂ LiCeI ₆	0.935	0.459
131.	Cs ₂ LiPrI ₆	0.938	0.450
132.	Cs ₂ LiNdI ₆	0.939	0.446
133.	Cs ₂ LiPmI ₆	0.941	0.441
134.	Cs ₂ LiSmI ₆	0.943	0.435
135.	Cs ₂ LiEuI ₆	0.945	0.430
136.	Cs ₂ LiGdI ₆	0.946	0.426
137.	Cs ₂ LiTbI ₆	0.948	0.419
138.	Cs ₂ LiDyI ₆	0.950	0.414
139.	Cs ₂ LiHoI ₆ *	0.952	0.409
140.	Cs ₂ NaLaI ₆	0.894	0.469
141.	Cs ₂ NaCeI ₆	0.897	0.459
142.	Cs ₂ NaPrI ₆	0.900	0.45
143.	Cs ₂ NaNdI ₆	0.901	0.446
144.	Cs ₂ NaPmI ₆	0.903	0.441
145.	Cs ₂ NaSmI ₆	0.904	0.435
146.	Cs ₂ NaEuI ₆	0.906	0.430

147.	Cs ₂ NaGdI ₆	0.907	0.426
148.	Cs ₂ NaTbI ₆	0.909	0.419
149.	Cs ₂ NaDyI ₆	0.911	0.414
150.	Cs ₂ NaHoI ₆	0.913	0.409
151.	Cs ₂ AgLaI ₆	0.877	0.469
152.	Cs ₂ AgCeI ₆	0.850	0.459
153.	Cs ₂ AgPrI ₆	0.882	0.450
154.	Cs ₂ AgNdI ₆	0.883	0.446
155.	Cs ₂ AgPmI ₆	0.885	0.441
156.	Cs ₂ AgSmI ₆	0.887	0.435
157.	Cs ₂ AgEuI ₆	0.888	0.430
158.	Cs ₂ AgGdI ₆	0.889	0.426
159.	Cs ₂ AgTbI ₆	0.891	0.419
160.	Cs ₂ AgDyI ₆	0.893	0.414
161.	Cs ₂ AgHoI ₆	0.894	0.409
162.	Cs ₂ KLaI ₆	0.847	0.469
163.	Cs ₂ KCeI ₆	0.850	0.459
164.	Cs ₂ KPrI ₆	0.852	0.450
165.	Cs ₂ KNdI ₆	0.853	0.446
166.	Cs ₂ KPmI ₆	0.854	0.441
167.	Cs ₂ KSmI ₆	0.856	0.435
168.	Cs ₂ KEuI ₆	0.857	0.430
169.	Cs ₂ KGdI ₆	0.859	0.426
170.	Cs ₂ KTbI ₆	0.861	0.419
171.	Cs ₂ KDyI ₆	0.862	0.414
172.	Cs ₂ KHoI ₆	0.863	0.409
173.	Cs ₂ TlLaI ₆	0.832	0.469
174.	Cs ₂ TlCeI ₆	0.835	0.459
175.	Cs ₂ TlPrI ₆	0.837	0.450
176.	Cs ₂ TlNdI ₆	0.838	0.446
177.	Cs ₂ TlPmI ₆	0.840	0.441
178.	Cs ₂ TlSmI ₆	0.841	0.435
179.	Cs ₂ TlEuI ₆	0.842	0.430
180.	Cs ₂ TlGdI ₆	0.844	0.426
181.	Cs ₂ TlTbI ₆	0.846	0.419
182.	Cs ₂ TlDyI ₆	0.847	0.414
183.	Cs ₂ TlHoI ₆	0.848	0.409
184.	Tl ₂ LiLaI ₆	0.890	0.469
185.	Tl ₂ LiCeI ₆	0.894	0.459
186.	Tl ₂ LiPrI ₆	0.897	0.450
187.	Tl ₂ LiNdI ₆	0.898	0.446
188.	Tl ₂ LiPmI ₆	0.899	0.441
189.	Tl ₂ LiSmI ₆	0.901	0.435
190.	Tl ₂ LiEuI ₆	0.903	0.430
191.	Tl ₂ LiGdI ₆	0.904	0.426
192.	Tl ₂ LiTbI ₆	0.906	0.419
193.	Tl ₂ LiDyI ₆	0.908	0.414
194.	Tl ₂ LiHoI ₆	0.910	0.409
195.	Tl ₂ NaLaI ₆	0.855	0.469
196.	Tl ₂ NaCeI ₆	0.857	0.459

197.	Tl ₂ NaPrI ₆	0.860	0.450
198.	Tl ₂ NaNdI ₆	0.861	0.446
199.	Tl ₂ NaPmI ₆	0.863	0.441
200.	Tl ₂ NaSmI ₆	0.864	0.435
201.	Tl ₂ NaEuI ₆	0.866	0.430
202.	Tl ₂ NaGdI ₆	0.867	0.426
203.	Tl ₂ NaTbI ₆	0.869	0.419
204.	Tl ₂ NaDyI ₆	0.871	0.414
205.	Tl ₂ NaHoI ₆	0.872	0.409
206.	Tl ₂ AgLaI ₆	0.838	0.469
207.	Tl ₂ AgCeI ₆	0.840	0.459
208.	Tl ₂ AgPrI ₆	0.843	0.450
209.	Tl ₂ AgNdI ₆	0.844	0.446
210.	Tl ₂ AgPmI ₆	0.846	0.441
211.	Tl ₂ AgSmI ₆	0.847	0.435
212.	Tl ₂ AgEuI ₆	0.849	0.430
213.	Tl ₂ AgGdI ₆	0.850	0.426
214.	Tl ₂ AgTbI ₆	0.852	0.419
215.	Tl ₂ AgDyI ₆	0.853	0.414
216.	Tl ₂ AgHoI ₆	0.855	0.409
217.	Tl ₂ KLaI ₆	0.810	0.469
218.	Tl ₂ KCeI ₆	0.812	0.459
219.	Tl ₂ KPrI ₆	0.814	0.450
220.	Tl ₂ KNdI ₆	0.815	0.446
221.	Tl ₂ KPmI ₆	0.817	0.441
222.	Tl ₂ KSmI ₆	0.818	0.435
223.	Tl ₂ KEuI ₆	0.820	0.430
224.	Tl ₂ KGdI ₆	0.821	0.426
225.	Tl ₂ KTbI ₆	0.823	0.419
226.	Tl ₂ KDyI ₆	0.824	0.414
227.	Tl ₂ KHoI ₆	0.825	0.409
228.	MA ₂ NaYI ₆	0.978	0.409
229.	MA ₂ KYI ₆	0.925	0.409
230.	MA ₂ TiYI ₆	0.909	0.409
231.	MA ₂ LiBiI ₆	0.998	0.468
232.	MA ₂ NaBiI ₆	0.958	0.468
233.	MA ₂ AgBiI ₆ *	0.939	0.468
234.	MA ₂ KBiI ₆	0.907	0.468
235.	MA ₂ TlBiI ₆	0.892	0.468
236.	MA ₂ LiLaI ₆	0.998	0.469
237.	MA ₂ LiCeI ₆	1.001	0.459
238.	MA ₂ LiPrI ₆	1.005	0.45
239.	MA ₂ LiNdI ₆	1.006	0.446
240.	MA ₂ LiPmI ₆	1.008	0.441
241.	MA ₂ LiSmI ₆	1.010	0.435
242.	MA ₂ LiEuI ₆	1.012	0.430
243.	MA ₂ LiGdI ₆	1.013	0.426
244.	MA ₂ LiTbI ₆	1.016	0.419
245.	MA ₂ LiDyI ₆	1.018	0.414
246.	MA ₂ LiHoI ₆	1.020	0.409

247.	MA ₂ NaLaI ₆	0.958	0.469
248.	MA ₂ NaCeI ₆	0.961	0.459
249.	MA ₂ NaPrI ₆	0.964	0.450
250.	MA ₂ NaNdI ₆	0.965	0.446
251.	MA ₂ NaPmI ₆	0.967	0.441
252.	MA ₂ NaSmI ₆	0.969	0.435
253.	MA ₂ NaEuI ₆	0.971	0.430
254.	MA ₂ NaGdI ₆	0.972	0.426
255.	MA ₂ NaTbI ₆	0.974	0.419
256.	MA ₂ NaDyI ₆	0.976	0.414
257.	MA ₂ NaHoI ₆	0.977	0.409
258.	MA ₂ AgLaI ₆	0.939	0.469
259.	MA ₂ AgCeI ₆	0.942	0.459
260.	MA ₂ AgPrI ₆	0.945	0.450
261.	MA ₂ AgNdI ₆	0.946	0.446
262.	MA ₂ AgPmI ₆	0.948	0.441
263.	MA ₂ AgSmI ₆	0.950	0.435
264.	MA ₂ AgEuI ₆	0.951	0.430
265.	MA ₂ AgGdI ₆	0.952	0.426
266.	MA ₂ AgTbI ₆	0.954	0.419
267.	MA ₂ AgDyI ₆	0.956	0.414
268.	MA ₂ AgHoI ₆	0.958	0.409
269.	MA ₂ KLaI ₆	0.907	0.469
270.	MA ₂ KCeI ₆	0.910	0.459
271.	MA ₂ KPrI ₆	0.913	0.450
272.	MA ₂ KNdI ₆	0.914	0.446
273.	MA ₂ KPmI ₆	0.916	0.440
274.	MA ₂ KSmI ₆	0.917	0.435
275.	MA ₂ KEuI ₆	0.918	0.430
276.	MA ₂ KGdI ₆	0.920	0.426
277.	MA ₂ KTbI ₆	0.922	0.419
278.	MA ₂ KDyI ₆	0.923	0.414
279.	MA ₂ KHoI ₆	0.925	0.409
280.	MA ₂ TlLaI ₆	0.891	0.469
281.	MA ₂ TlCeI ₆	0.894	0.459
282.	MA ₂ TlPrI ₆	0.897	0.450
283.	MA ₂ TlNdI ₆	0.898	0.446
284.	MA ₂ TlPmI ₆	0.899	0.440
285.	MA ₂ TlSmI ₆	0.901	0.435
286.	MA ₂ TlEuI ₆	0.903	0.430
287.	MA ₂ TlGdI ₆	0.904	0.426
288.	MA ₂ TlTbI ₆	0.906	0.419
289.	MA ₂ TlDyI ₆	0.907	0.414
290.	MA ₂ TlHoI ₆	0.908	0.409
291.	FA ₂ KBiI ₆	0.982	0.468
292.	FA ₂ KLaI ₆	0.982	0.469
293.	FA ₂ KCeI ₆	0.985	0.459
294.	FA ₂ KPrI ₆	0.988	0.450
295.	FA ₂ KNdI ₆	0.989	0.446
296.	FA ₂ KPmI ₆	0.991	0.441

297.	FA ₂ KSml ₆	0.993	0.435
298.	FA ₂ KEul ₆	0.994	0.430
299.	FA ₂ KGdl ₆	0.995	0.426
300.	FA ₂ KTbl ₆	0.998	0.419
301.	FA ₂ KDyl ₆	0.999	0.414
302.	FA ₂ KHol ₆	1.001	0.409
303.	FA ₂ TIYl ₆	0.983	0.409
304.	FA ₂ TlLal ₆	0.965	0.469
305.	FA ₂ TlCel ₆	0.968	0.459
306.	FA ₂ TlPrI ₆	0.971	0.450
307.	FA ₂ TlNdl ₆	0.972	0.446
308.	FA ₂ TlPml ₆	0.973	0.441
309.	FA ₂ TlSml ₆	0.975	0.435
310.	FA ₂ TlEul ₆	0.977	0.430
311.	FA ₂ TlGdl ₆	0.978	0.426
312.	FA ₂ TlTbl ₆	0.980	0.419
313.	FA ₂ TlDyl ₆	0.982	0.414
314.	FA ₂ TlHol ₆	0.984	0.409

**Reported in the literature without structural data*