Band gap Engineering by Sublattice Mixing in $\text{Cs}_2\text{AgInCl}_6$: High-throughput Screening from First-principles

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Abstract

Lead-free double perovskite materials (viz. Cs$_2$AgInCl$_6$) are being explored as stable and non-toxic alternatives of lead halide perovskites. In order to expand the optical response of Cs$_2$AgInCl$_6$ in visible region, we report here the stability, electronic structure and optical properties of Cs$_2$AgInCl$_6$ by sublattice mixing of various elements. Here we have employed high-throughput screening using a hierarchical first-principles based approach starting from density functional theory (DFT) with appropriate exchange and correlation functionals to beyond DFT methods under the framework of many body perturbation theory (viz. G$_0$W$_0$@HSE06). We have started with 32 primary set of combinations of metals M(I), M(II), M(III) and halogen X at Ag/In and Cl site respectively, where concentration of each set is varied to build a database of nearly 140 combinations. The most suitable mixed sublattices are identified to engineer the band gap of Cs$_2$AgInCl$_6$ to have its application in optoelectronic devices under visible light.

Graphical TOC Entry

Keywords
double perovskite, Cs$_2$AgInCl$_6$, defects, hybrid DFT, stability, optical response
Lead halide perovskites APbX$_3$ ($A = \text{CH}_3\text{NH}_3^+, \text{HC(NH}_2\text{)}_2^+, \text{Cs}^+, \text{and } X = \text{Cl}^-, \text{Br}^-, \text{I}^-$) have created a huge sensation in the field of optoelectronics, particularly photovoltaics owing to their suitable optical band gap, long carrier diffusion length, high carrier mobility and low manufacturing cost.$^{1–8}$ Moreover, the band gap is tunable with high defect tolerance.$^{9–11}$ These materials find applications in various optoelectronic devices, namely, solar cells,$^2,12–14$ light emitting diodes,$^{15,16}$ lasers$^{17,18}$ and photodetectors.$^{19,20}$ In spite of their great potential in a vast number of applications, there are two major challenges: (i) instability against exposure to humidity, heat or light and (ii) toxicity of Pb. These have posed hindrance in their commercialization. To tackle these issues, many works have been endeavored to find alternative stable and environmentally sustainable metal halide perovskites with fascinating optoelectronic properties akin to lead halide perovskites.$^{21–25}$

One of the approaches for removing toxicity is to replace Pb$^{2+}$ with some other divalent metal. However, the replacement using other group divalent cations results in either indirect or large band gap materials with degraded optoelectronic properties.$^{26–29}$ Substitution of group 14 divalent cations, viz. Sn$^{2+}$ and Ge$^{2+}$ have also been synthesized by researchers, but these are not stable at ambient conditions due to the easy oxidation to tetravalent Sn$^{4+}$ and Ge$^{4+}$, respectively.$^{30,31}$ Another promising approach is to substitute a monovalent M(I) and a trivalent M(III) metal alternatively in place of two divalent Pb, that forms the double perovskite $A_2M(I)M(III)X_6$. Recently, lead-free metal halide double perovskites have been synthesized, which are stable and environmentally benign, viz. Cs$_2$AgBiX$_6$ ($X = \text{Cl}^-, \text{Br}^-, \text{I}^-$) and Cs$_2$AgInCl$_6$.$^{32–39}$ Cs$_2$AgBiX$_6$ perovskites possess indirect band gap, which results in weaker absorption and high non-radiative recombination loss.$^{32–34}$ In contrast, Cs$_2$AgInCl$_6$ has direct band gap. However, its wide band gap (3.3 eV) does not show optical response in visible region.$^{36,37}$ Alloying with suitable elements could be the best solution to reduce its band gap and expand the spectral response in visible light region.

In this Letter, we have done the sublattice mixing by partial substitution of several metals M(I), M(II), M(III) and halogen X at Ag/In and Cl site, respectively, to reduce the band
The double perovskite $\text{Cs}_2\text{AgInCl}_6$ has a cubic structure with space group $Fm\bar{3}m$. The corresponding sublattice is composed of alternate octahedra of $\text{InCl}_6$ and $\text{AgCl}_6$ as shown in Figure 1a. On partial substitution of different elements as shown in Figure 1b (metals
and/or halogens), the distortion is very less pronounced. Here we have started with 32 primary set of combinations of metals M(I), M(II), M(III) and halogen X at Ag/In and Cl site respectively, where concentration of each set is varied to build a database of nearly 140 combinations. However, note that here, we have presented the results of 25% substitution for metals and 4% substitution for halogen atoms. This is because we have seen and thoroughly checked that, as we increase the concentration of the external element, if the band gap is increased (or decreased), it increases (or decreases) consistently on further increasing the concentration. Two such test cases are shown in Figure S1 in Supporting Information (SI). We have also reported this, to be the case in our previous experimental finding.\(^{46}\) The structural stability of all the alloyed configurations has been determined by calculating two geometrical parameters, viz. the Goldschmidt tolerance factor \((t)\) and the octahedral factor \((\mu)\). For single perovskite \(\text{ABX}_3\), \(t = (r_A + r_X) / \sqrt{2}(r_B + r_X)\) and \(\mu = r_B / r_X\), where \(r_A\), \(r_B\), and \(r_X\) are the ionic radii of cation A, B, and anion X, respectively. In case of double perovskites, \(r_B\) is the average of the ionic radii at B sites. For stable perovskites, the ranges of \(t\) and \(\mu\) are respectively, \(0.8 \leq t \leq 1.0\) and \(\mu > 0.41.\)\(^{47}\) The Shannon ionic radii\(^ {48}\) have been considered to evaluate \(t\) and \(\mu\). For the configurations we have considered, \(t\) lies between 0.85 and 0.91, and \(\mu\) has the value between 0.50 and 0.59 (see Table S1). Therefore, these probable structures are stable.

In order to determine the thermodynamic stability, we have computed the decomposition enthalpy \((\Delta H_D)\) using PBE and HSE06 xc functionals. We have alloyed the external elements in \(\text{Cs}_8\text{Ag}_4\text{In}_4\text{Cl}_{24}\) supercell framework to model a solid solution. The \(\Delta H_D\) for the decomposition of \(\text{Cs}_8\text{Ag}_4\text{In}_4\text{Cl}_{24}\) into binary compounds is calculated as follows:

\[
\Delta H_D(\text{Cs}_8\text{Ag}_4\text{In}_4\text{Cl}_{24}) = E(\text{Cs}_8\text{Ag}_4\text{In}_4\text{Cl}_{24}) - 8E(\text{CsCl}) - 4E(\text{AgCl}) - 4E(\text{InCl}_3),
\]

where \(E(\text{Cs}_8\text{Ag}_4\text{In}_4\text{Cl}_{24})\), \(E(\text{CsCl})\), \(E(\text{AgCl})\), and \(E(\text{InCl}_3)\) are the DFT energies of the respective compounds. The alloyed configurations having negative value of the \(\Delta H_D\) are
stable. Figure 2a and 2b show the decomposition enthalpy for decomposition of (un)alloyed Cs$_2$AgInCl$_6$ into binary compounds using PBE and HSE06 xc functionals, respectively (decomposition pathways are shown in SI). Only those elements, which lead to decrement in band gap using PBE xc functional, are further considered with HSE06 xc functional. Note that, Tl(III), Cd(II), and Pb(II) are not considered here due to toxicity. The quaternary compounds can be decomposed into ternary compounds. Therefore, we have also considered those pathways for the materials (see decomposition pathways in SI), which have the favorable band gap. The decomposition enthalpy for decomposition of (un)alloyed Cs$_2$AgInCl$_6$ into ternary compounds is shown in Figure 2c. For decomposition of Cs$_8$Ag$_4$In$_4$Cl$_{24}$ into ternary compounds, the $\Delta H_D$ is determined as follows:

$$
\Delta H_D(Cs_8Ag_4In_4Cl_{24}) = E(Cs_8Ag_4In_4Cl_{24}) - 2E(CsAgCl_2) - 2E(Cs_3In_2Cl_9) - 2E(AgCl). \quad (2)
$$

Figure 2: Decomposition enthalpy ($\Delta H_D$) vs band gap for decomposition of pristine and alloyed configurations into binary compounds using the xc functionals (a) PBE and (b) HSE06, and (c) decomposition into ternary compounds using HSE06 xc functional.

The $\Delta H_D$ has the value of $-0.248$ eV/atom and $-0.010$ eV/atom for the decomposition of Cs$_8$Ag$_4$In$_4$Cl$_{24}$ into binary and ternary compounds, respectively. These negative values confirm that the perovskite Cs$_8$Ag$_4$In$_4$Cl$_{24}$ is stable. We have found that all the selected elements for sublattice mixing are stable with respect to the decomposition into binary compounds (see Table S1). However, for ternary decomposition pathway, Co(II), Ni(II), and Cu(II) are not stable (see Figure 2c). This may be attributed to the smaller size of
these cations that are unable to accommodate two octahedra with Cl$_6$. Note that Ni(II) and Cu(II) have the lowest octahedral factor (see Table S1). Also, Cu(I) and Ga(III) are less stable than pristine (see Figure 2c).

A screening of various atoms for sublattice mixing has been done by calculating the band gap first using generalized gradient approximation (PBE). For pristine Cs$_2$AgInCl$_6$, the band gap using PBE xc functional comes out to be 0.95 eV. Further, to see the effect of spin-orbit coupling (SOC) in this material, we have also calculated the band gap using PBE+SOC, which gives a value of 0.93 eV. This implies that SOC has insignificant effect on the electronic properties of Cs$_2$AgInCl$_6$. This corroborates with the fact that it does not contain any heavy element like Pb or Bi, where some significant effect of SOC is expected in the electronic properties of such materials. Therefore, we have ignored the effect of SOC in our further calculations as the atoms we have considered for substitution are not heavy elements. However, the band gap is highly underestimated by PBE xc functional due to the well known self interaction error. Therefore, we have further performed the calculations using more advanced hybrid xc functional HSE06 for those mixed sublattices, where in comparison to pristine, the band gap was reduced (see Figure 2a, 2b, and Table S1). The calculated value of band gap for Cs$_2$AgInCl$_6$ is 2.31 eV, which is in good agreement with previously reported theoretical value, but still underestimated in comparison to the experimental value (3.3 eV). In case of Cu(I) and Au(I) substitutional alloying at Ag site, the band gap is reduced by $\sim 0.8$ eV, having a value of 1.51 eV and 1.54 eV, respectively. On the other hand, in case of substitution of M(III) at In site, it does not have much effect on reduction in band gap. Only Co(III) and Ir(III) substitutional alloying are able to reduce the band gap from 2.31 eV to 2.08 eV, whereas the rest are either increasing it or have no effect on the band gap. In case of M(II) substitutional alloying, one at Ag and other one at In site, only Zn(II), and Mn(II) are able to reduce the band gap effectively, having a band gap value of 1.87 eV and 1.77 eV, respectively. In case of halogen substitution viz. Br and I, it helps to reduce the band gap to 2.10 and 1.85 eV, respectively (see Table S1).
Figure 3: Atom projected partial density of states (pDOS) using HSE06 xc functional of (a) pristine Cs$_2$AgInCl$_6$, (b) Cs$_2$AgGa$_{0.25}$In$_{0.75}$Cl$_6$, (c) Cs$_2$Cu$_{0.25}$Ag$_{0.75}$InCl$_6$, (d) Cs$_2$Au$_{0.25}$Ag$_{0.75}$InCl$_6$, (e) Cs$_2$Zn$_{0.50}$Ag$_{0.75}$In$_{0.75}$Cl$_6$, (f) Cs$_2$Mn$_{0.50}$Ag$_{0.75}$In$_{0.75}$Cl$_6$, (g) Cs$_2$AgInBr$_{0.04}$Cl$_{5.96}$, and (h) Cs$_2$AgInI$_{0.04}$Cl$_{5.96}$. 
The reduction in band gap can be explained by observing the atom projected partial density of states (pDOS) (see Figure 3). In the pristine $\text{Cs}_2\text{AgInCl}_6$, the Cl p-orbitals and Ag d-orbitals contribute to the valence band maximum (VBM), whereas the In and Ag s-orbitals contribute to the conduction band minimum (CBm) (see Figure 3a). The states are symmetric with respect to the spin alignments (spin up or down) indicating that the electrons are paired. In case of substitutional alloying of Cu(I) and Au(I), their d-orbitals have more energy than the Ag d-orbitals and hence, reduce the band gap by elevating the VBM (see Figure 3c and 3d). However, in case of the M(III) substitution at In site, generally, the states lie inside the valence band (VB) or the conduction band (CB), and thus, do not reduce the band gap effectively. From Figure 3b, we can see that the Ga(III) is reducing the band gap by a negligible amount (as the states contributed by the Ga are lying inside VB and CB). Whereas, the Co(III) and Ir(III) substitution at In site show a finite decrease in the band gap. This is due to the Co d-orbitals and Ir d-orbitals contribution at CBm and VBM, respectively (see Figure S2). In case of M(II), there is a little contribution from d- and s-orbitals of M(II) at VB and CBm, respectively, and therefore, reducing the band gap by introducing the shallow states (see Figure 3e and 3f). The band gap reduction on substituting Br/I at Cl site is occurred by elevating the VBM, which is due to Br/I p-orbitals contribution at VBM (see Figure 3g and 3h). In all these cases, the defect levels are shallow, which is a desirable property for optoelectronic devices. Shallow defect states ensure that the recombination of photogenerated charge carriers is not prominent and thus, the decrement in charge carrier mobility and diffusion will be insignificant.

To obtain the optical properties, that are crucial for the perovskite to be used in optoelectronic devices, we have calculated the frequency dependent complex dielectric function $\varepsilon(\omega) = \text{Re}(\varepsilon(\omega)) + \text{Im}(\varepsilon(\omega))$ using G0W0@HSE06 (the results with HSE06 xc functional are shown in Figure S3). Figure 4(a) and 4(b) show the imaginary [$\text{Im}(\varepsilon)$] and real [$\text{Re}(\varepsilon)$] part of the dielectric function, respectively. The real static part (at $\omega = 0$) of the dielectric function is a direct measure of refractive index. Higher the refractive index, better will be
the probability to absorb light. On alloying, the refractive index is increased, and thus, the optical properties are enhanced. Its value is varying from 2.46 – 2.88. The static Re $\varepsilon$ is 2.46 for pristine Cs$_2$AgInCl$_6$, and increased on alloying (see Figure 4b, Figure S4 and Table S2). The imaginary part reflects the transitions from occupied to unoccupied bands. The imaginary absorption edge and onset are red shifted and hence, the visible light response is induced on alloying (see Figure 4a). Figure 4c shows the absorption coefficient $\alpha(\omega)$, which is related to real and imaginary part of the dielectric function as follows:

$$\alpha(\omega) = \sqrt{2} \omega \left( \sqrt{\text{Re}(\varepsilon(\omega))^2 + \text{Im}(\varepsilon(\omega))^2} - \text{Re}(\varepsilon(\omega)) \right)^{\frac{1}{2}}. \quad (3)$$

We have seen that on alloying, the peaks of the absorption spectra are red shifted and hence, these mixed sublattices display response in the visible light. This response is attributed to
the reduction in band gap as shown in Figure 4d.

In conclusion, we have investigated the role of metals M(I), M(II), M(III) and halogen X in alloyed Cs$_2$AgInCl$_6$ for inducing the visible light response by tuning its electronic properties for optoelectronic devices using state of the art DFT and beyond DFT methods. We have found that the Goldschmidt tolerance factor and octahedron factor lie in the suitable range to form stable perovskite structure. The decomposition enthalpy of all the mixed sublattices is negative with respect to the binary decomposition indicating that the alloyed systems will not decompose into their binary precursors and thus, are thermodynamically stable. However, Co(II), Ni(II), and Cu(II) are thermodynamically unstable and could decompose into ternary compounds. We have observed that SOC effect is negligible in the double perovskite Cs$_2$AgInCl$_6$ as it does not contain any heavy element like Lead (Pb) and Bismuth (Bi). Many partial substitutional alloying configurations help in reducing the band gap to desired range and thus, increasing the absorption. We have inferred that the sublattices with Cu(I) and Au(I) at Ag site, Co(III) and Ir(III) at In site, Zn(II) at Ag and In site simultaneously, Mn(II) at Ag and In site simultaneously, and Br and I substitution at Cl site as the most promising candidates for various optoelectronic devices.

**Computational Methods**

The density functional theory (DFT)\textsuperscript{40,41} calculations have been performed using the Vienna \textit{ab initio} simulation package (VASP).\textsuperscript{49,50} The ion-electron interactions in all the elemental constituents are described using projector-augmented wave (PAW) potentials.\textsuperscript{50,51} All the structures are optimized (i.e. the atomic positions are relaxed) using generalized gradient approximation as implemented in PBE\textsuperscript{42} exchange-correlation (xc) functional until the forces are smaller than 0.001 eV/Å. The electronic self consistency loop convergence is set to 0.01 meV, and the kinetic energy cutoff is set to 500 eV for plane wave basis set expansion. A k-point mesh of 4 × 4 × 4 is used for Brillouin zone integration, which is generated using
Monkhorst-Pack\textsuperscript{52} scheme. Advanced hybrid xc functional HSE06\textsuperscript{43} is used for the better estimation of band gap as well as thermodynamic stability. For determination of the optical properties, single shot GW\textsuperscript{44,45} ($G_0W_0$) calculations have been performed on top of the orbitals obtained from HSE06 xc functional. The polarizability calculations are carried out on a grid of 50 frequency points. The number of unoccupied bands is set to four times the number of occupied orbitals. Note that spin-orbit coupling (SOC) is not taken into account because it negligibly affects the electronic structure of Ag/In-based halide double perovskite, which is consistent with previous studies.\textsuperscript{53,54}

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Band gap engineering by sublattice mixing in \( \text{Cs}_2\text{AgInCl}_6 \): High-throughput screening from first-principles

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I. Change in band gap on increasing concentration of the dopants

II. Tolerance factor, octahedral factor, band gap and decomposition enthalpy (decomposition into binary compounds) using PBE and HSE06 xc functional of (un)doped Cs$_2$AgInCl$_6$

III. Reactions for decomposition of pristine and doped Cs$_2$AgInCl$_6$ into binary/ternary compounds

IV. Density of states of Cs$_2$AgCo$_{0.25}$In$_{0.75}$Cl$_6$ and Cs$_2$AgIr$_{0.25}$In$_{0.75}$Cl$_6$

V. Optical properties of (un)doped Cs$_2$AgInCl$_6$ using HSE06 xc functional

VI. Optical properties of Cs$_2$AgCo$_{0.25}$In$_{0.75}$Cl$_6$ and Cs$_2$AgIr$_{0.25}$In$_{0.75}$Cl$_6$ using G$_0$W$_0$@HSE06

VII. Dielectric constant ($\varepsilon_\infty$) of un(doped) Cs$_2$AgInCl$_6$ using G$_0$W$_0$@HSE06
Figure S1: Change in band gap on increasing concentration of the impurity atoms.
Table S1: Tolerance factor, octahedral factor, band gap and decomposition enthalpy (decomposition into binary compounds) using PBE and HSE06 xc functional of different configurations

| Configuration | Tolerance factor ($t$) | Octahedral factor ($\mu$) | Band gap (PBE) (eV) | $\Delta H_D$ (binary decomposition) (PBE) (eV/atom) | Band gap HSE06 (eV) | $\Delta H_D$ (binary decomposition) (HSE06) (eV/atom) |
|---------------|------------------------|--------------------------|---------------------|--------------------------------------------------|-------------------|--------------------------------------------------|
| Cs$_2$AgInCl$_6$ | 0.88                   | 0.54                     | 0.95                | -0.233                                           | 2.31              | -0.248                                           |
| Cs$_2$Cu$_{0.25}$Ag$_{0.75}$InCl$_6$ | 0.90                   | 0.51                     | 0.04                | -0.224                                           | 1.51              | -0.237                                           |
| Cs$_2$Au$_{0.25}$Ag$_{0.75}$InCl$_6$ | 0.87                   | 0.55                     | 0.32                | -0.212                                           | 1.54              | -0.228                                           |
| Cs$_2$Na$_{0.25}$Ag$_{0.75}$InCl$_6$ | 0.89                   | 0.53                     | 1.22                | -0.232                                           |                   |                                                  |
| Cs$_2$K$_{0.25}$Ag$_{0.75}$InCl$_6$ | 0.87                   | 0.55                     | 1.37                | -0.216                                           |                   |                                                  |
| Cs$_2$Rb$_{0.25}$Ag$_{0.75}$InCl$_6$ | 0.87                   | 0.56                     | 1.43                | -0.200                                           |                   |                                                  |
| Cs$_2$AgAl$_{0.25}$In$_{0.75}$Cl$_6$ | 0.89                   | 0.52                     | 1.03                | -0.196                                           |                   |                                                  |
| Cs$_2$AgGa$_{0.25}$In$_{0.75}$Cl$_6$ | 0.89                   | 0.53                     | 0.87                | -0.192                                           | 2.23              | -0.202                                           |
| Cs$_2$AgTi$_{0.25}$In$_{0.75}$Cl$_6$ | 0.88                   | 0.54                     | 0.37                | -0.218                                           |                   |                                                  |
| Cs$_2$AgCo$_{0.25}$In$_{0.75}$Cl$_6$ | 0.89                   | 0.52                     | 0.73                | -0.217                                           | 2.09              | -0.230                                           |
| Cs$_2$AgRh$_{0.25}$In$_{0.75}$Cl$_6$ | 0.89                   | 0.53                     | 0.91                | -0.195                                           | 2.53              | -0.204                                           |
| Cs$_2$AgIr$_{0.25}$In$_{0.75}$Cl$_6$ | 0.89                   | 0.53                     | 0.43                | -0.191                                           | 2.08              | -0.202                                           |
| Cs$_2$AgSc$_{0.25}$In$_{0.75}$Cl$_6$ | 0.89                   | 0.53                     | 1.37                | -0.200                                           |                   |                                                  |
| Cs$_2$AgY$_{0.25}$In$_{0.75}$Cl$_6$ | 0.88                   | 0.54                     | 1.54                | -0.194                                           |                   |                                                  |
| Cs$_2$AgLa$_{0.25}$In$_{0.75}$Cl$_6$ | 0.87                   | 0.55                     | 1.89                | -0.178                                           |                   |                                                  |
| Cs$_2$AgAc$_{0.25}$In$_{0.75}$Cl$_6$ | 0.87                   | 0.56                     | 1.78                | -0.161                                           |                   |                                                  |
| Cs$_2$AgCr$_{0.25}$In$_{0.75}$Cl$_6$ | 0.89                   | 0.53                     | 1.06                | -0.197                                           |                   |                                                  |
| Cs$_2$AgSb$_{0.25}$In$_{0.75}$Cl$_6$ | 0.89                   | 0.54                     | 1.72                | -0.197                                           |                   |                                                  |
| Cs$_2$AgBi$_{0.25}$In$_{0.75}$Cl$_6$ | 0.87                   | 0.55                     | 1.96                | -0.200                                           |                   |                                                  |
| Cs$_2$Ca$_{0.50}$Ag$_{0.50}$In$_{0.75}$Cl$_6$ | 0.88                   | 0.54                     | 1.89                | -0.177                                           |                   |                                                  |
| Cs$_2$Sr$_{0.50}$Ag$_{0.50}$In$_{0.75}$Cl$_6$ | 0.87                   | 0.57                     | 2.11                | -0.148                                           |                   |                                                  |
| Cs$_2$Ba$_{0.50}$Ag$_{0.50}$In$_{0.75}$Cl$_6$ | 0.85                   | 0.59                     | 2.29                | -0.096                                           |                   |                                                  |
| Cs$_2$Zn$_{0.50}$Ag$_{0.50}$In$_{0.75}$Cl$_6$ | 0.90                   | 0.51                     | 0.61                | -0.176                                           | 1.87              | -0.186                                           |
| Cs$_2$Cd$_{0.50}$Ag$_{0.50}$In$_{0.75}$Cl$_6$ | 0.89                   | 0.54                     | 0.64                | -0.180                                           |                   |                                                  |
| Cs$_2$Ge$_{0.50}$Ag$_{0.50}$In$_{0.75}$Cl$_6$ | 0.90                   | 0.50                     | 1.43                | -0.196                                           |                   |                                                  |
| Cs$_2$Sn$_{0.50}$Ag$_{0.50}$In$_{0.75}$Cl$_6$ | 0.87                   | 0.57                     | 1.18                | -0.176                                           |                   |                                                  |
| Cs$_2$Pb$_{0.50}$Ag$_{0.50}$In$_{0.75}$Cl$_6$ | 0.87                   | 0.57                     | 1.72                | -0.160                                           |                   |                                                  |
| Cs$_2$Mn$_{0.50}$Ag$_{0.50}$In$_{0.75}$Cl$_6$ | 0.90                   | 0.52                     | 0.31                | -0.187                                           | 1.77              | -0.194                                           |
| Cs$_2$Co$_{0.50}$Ag$_{0.50}$In$_{0.75}$Cl$_6$ | 0.90                   | 0.51                     | metallic            | -0.166                                           | 0.95              | -0.140                                           |
| Cs$_2$Ni$_{0.50}$Ag$_{0.50}$In$_{0.75}$Cl$_6$ | 0.91                   | 0.50                     | metallic            | -0.160                                           | 1.98              | -0.168                                           |
| Cs$_2$Cu$_{0.50}$Ag$_{0.50}$In$_{0.75}$Cl$_6$ | 0.90                   | 0.50                     | metallic            | -0.172                                           | 1.89              | -0.140                                           |
| Cs$_2$AgInBr$_{0.04}$Cl$_{5.96}$ | 0.88                   | 0.54                     | 0.80                | -0.226                                           | 2.10              | -0.242                                           |
| Cs$_2$AgInI$_{0.04}$Cl$_{5.96}$ | 0.88                   | 0.54                     | 0.64                | -0.206                                           | 1.85              | -0.224                                           |
Reactions for decomposition of pristine and doped Cs$_2$AgInCl$_6$ into binary/ternary compounds:

(1) Cs$_2$AgInCl$_6$

Cs$_8$Ag$_4$In$_4$Cl$_{24}$ → 8 CsCl + 4 AgCl + 4 InCl$_3$

Cs$_8$Ag$_4$In$_4$Cl$_{24}$ → 2 CsAgCl$_2$ + 2 Cs$_3$In$_2$Cl$_9$ + 2 AgCl

(2) Cs$_2$Cu$_{0.25}$Ag$_{0.75}$InCl$_6$

Cs$_8$Cu$_1$Ag$_3$In$_4$Cl$_{24}$ → 8 CsCl + 3 AgCl + CuCl + 4 InCl$_3$

Cs$_8$Cu$_1$Ag$_3$In$_4$Cl$_{24}$ → $\frac{1}{2}$ CsCu$_2$Cl$_3$ + 2 Cs$_3$In$_2$Cl$_9$ + 3 AgCl + $\frac{3}{2}$ CsCl

(3) Cs$_2$Au$_{0.25}$Ag$_{0.75}$InCl$_6$

Cs$_8$Au$_1$Ag$_3$In$_4$Cl$_{24}$ → 8 CsCl + 3 AgCl + AuCl + 4 InCl$_3$

(4) Cs$_2$Na$_{0.25}$Ag$_{0.75}$InCl$_6$

Cs$_8$Na$_1$Ag$_3$In$_4$Cl$_{24}$ → 8 CsCl + 3 AgCl + NaCl + 4 InCl$_3$

(5) Cs$_2$K$_{0.25}$Ag$_{0.75}$InCl$_6$

Cs$_8$K$_1$Ag$_3$In$_4$Cl$_{24}$ → 8 CsCl + 3 AgCl + KCl + 4 InCl$_3$

(6) Cs$_2$Rb$_{0.25}$Ag$_{0.75}$InCl$_6$

Cs$_8$Rb$_1$Ag$_3$In$_4$Cl$_{24}$ → 8 CsCl + 3 AgCl + RbCl + 4 InCl$_3$

(7) Cs$_2$AgAl$_{0.25}$In$_{0.75}$Cl$_6$

Cs$_8$Ag$_4$Al$_1$In$_3$Cl$_{24}$ → 8 CsCl + 4 AgCl + 3 InCl$_3$ + AlCl$_3$

(8) Cs$_2$AgGa$_{0.25}$In$_{0.75}$Cl$_6$

Cs$_8$Ag$_4$Ga$_1$In$_3$Cl$_{24}$ → 8 CsCl + 4 AgCl + 3 InCl$_3$ + GaCl$_3$

Cs$_8$Ag$_4$Ga$_1$In$_3$Cl$_{24}$ → CsGaCl$_4$ + $\frac{3}{2}$ Cs$_3$In$_2$Cl$_9$ + 4 AgCl + $\frac{5}{2}$ CsCl

(9) Cs$_2$AgTl$_{0.25}$In$_{0.75}$Cl$_6$
Cs₈Ag₄TlIn₃Cl₂₄ → 8 CsCl + 4 AgCl + 3 InCl₃ + TlCl₃
(10) Cs₂AgCo₀.₂₅In₀.₇₅Cl₆
Cs₈Ag₄Co₁In₃Cl₂₄ → 8 CsCl + 4 AgCl + 3 InCl₃ + CoCl₃
(11) Cs₂AgRh₀.₂₅In₀.₇₅Cl₆
Cs₈Ag₄Rh₁In₃Cl₂₄ → 8 CsCl + 4 AgCl + 3 InCl₃ + RhCl₃
(12) Cs₂AgIr₀.₂₅In₀.₇₅Cl₆
Cs₈Ag₄Ir₁In₃Cl₂₄ → 8 CsCl + 4 AgCl + 3 InCl₃ + IrCl₃
(13) Cs₂AgSc₀.₂₅In₀.₇₅Cl₆
Cs₈Ag₄Sc₁In₃Cl₂₄ → 8 CsCl + 4 AgCl + 3 InCl₃ + ScCl₃
(14) Cs₂AgY₀.₂₅In₀.₇₅Cl₆
Cs₈Ag₄Y₁In₃Cl₂₄ → 8 CsCl + 4 AgCl + 3 InCl₃ + YCl₃
(15) Cs₂AgLa₀.₂₅In₀.₇₅Cl₆
Cs₈Ag₄La₁In₃Cl₂₄ → 8 CsCl + 4 AgCl + 3 InCl₃ + LaCl₃
(16) Cs₂AgAc₀.₂₅In₀.₇₅Cl₆
Cs₈Ag₄Ac₁In₃Cl₂₄ → 8 CsCl + 4 AgCl + 3 InCl₃ + AcCl₃
(17) Cs₂AgCr₀.₂₅In₀.₇₅Cl₆
Cs₈Ag₄Cr₁In₃Cl₂₄ → 8 CsCl + 4 AgCl + 3 InCl₃ + CrCl₃
(18) Cs₂AgSb₀.₂₅In₀.₇₅Cl₆
Cs₈Ag₄Sb₁In₃Cl₂₄ → 8 CsCl + 4 AgCl + 3 InCl₃ + SbCl₃
(19) Cs₂AgBi₀.₂₅In₀.₇₅Cl₆
Cs₈Ag₄Bi₁In₃Cl₂₄ → 8 CsCl + 4 AgCl + 3 InCl₃ + BiCl₃
(20) Cs₂Ca₀.₅₀Ag₀.₇₅In₀.₇₅Cl₆
Cs\textsubscript{8}Ca\textsubscript{2}Ag\textsubscript{3}In\textsubscript{3}Cl\textsubscript{24} \rightarrow 8 \text{CsCl} + 3 \text{AgCl} + 3 \text{InCl}_3 + 2 \text{CaCl}_2

(21) \text{Cs}_2\text{Sr}_{0.50}\text{Ag}_{0.75}\text{In}_{0.75}\text{Cl}_6

Cs\textsubscript{8}Sr\textsubscript{2}Ag\textsubscript{3}In\textsubscript{3}Cl\textsubscript{24} \rightarrow 8 \text{CsCl} + 3 \text{AgCl} + 3 \text{InCl}_3 + 2 \text{SrCl}_2

(22) \text{Cs}_2\text{Ba}_{0.50}\text{Ag}_{0.75}\text{In}_{0.75}\text{Cl}_6

Cs\textsubscript{8}Ba\textsubscript{2}Ag\textsubscript{3}In\textsubscript{3}Cl\textsubscript{24} \rightarrow 8 \text{CsCl} + 3 \text{AgCl} + 3 \text{InCl}_3 + 2 \text{BaCl}_2

(23) \text{Cs}_2\text{Zn}_{0.50}\text{Ag}_{0.75}\text{In}_{0.75}\text{Cl}_6

Cs\textsubscript{8}Zn\textsubscript{2}Ag\textsubscript{3}In\textsubscript{3}Cl\textsubscript{24} \rightarrow 8 \text{CsCl} + 3 \text{AgCl} + 3 \text{InCl}_3 + 2 \text{ZnCl}_2

Cs\textsubscript{8}Zn\textsubscript{2}Ag\textsubscript{3}In\textsubscript{3}Cl\textsubscript{24} \rightarrow 2 \text{Cs}_2\text{ZnCl}_4 + \frac{1}{2} \text{Cs}_3\text{In}_2\text{Cl}_9 + 3 \text{AgCl} + \frac{5}{2} \text{CsCl} + 2 \text{InCl}_3

(24) \text{Cs}_2\text{Cd}_{0.50}\text{Ag}_{0.75}\text{In}_{0.75}\text{Cl}_6

Cs\textsubscript{8}Cd\textsubscript{2}Ag\textsubscript{3}In\textsubscript{3}Cl\textsubscript{24} \rightarrow 8 \text{CsCl} + 3 \text{AgCl} + 3 \text{InCl}_3 + 2 \text{CdCl}_2

(25) \text{Cs}_2\text{Ge}_{0.50}\text{Ag}_{0.75}\text{In}_{0.75}\text{Cl}_6

Cs\textsubscript{8}Ge\textsubscript{2}Ag\textsubscript{3}In\textsubscript{3}Cl\textsubscript{24} \rightarrow 8 \text{CsCl} + 3 \text{AgCl} + 3 \text{InCl}_3 + 2 \text{GeCl}_2

(26) \text{Cs}_2\text{Sn}_{0.50}\text{Ag}_{0.75}\text{In}_{0.75}\text{Cl}_6

Cs\textsubscript{8}Sn\textsubscript{2}Ag\textsubscript{3}In\textsubscript{3}Cl\textsubscript{24} \rightarrow 8 \text{CsCl} + 3 \text{AgCl} + 3 \text{InCl}_3 + 2 \text{SnCl}_2

(27) \text{Cs}_2\text{Pb}_{0.50}\text{Ag}_{0.75}\text{In}_{0.75}\text{Cl}_6

Cs\textsubscript{8}Pb\textsubscript{2}Ag\textsubscript{3}In\textsubscript{3}Cl\textsubscript{24} \rightarrow 8 \text{CsCl} + 3 \text{AgCl} + 3 \text{InCl}_3 + 2 \text{PbCl}_2

(28) \text{Cs}_2\text{Mn}_{0.50}\text{Ag}_{0.75}\text{In}_{0.75}\text{Cl}_6

Cs\textsubscript{8}Mn\textsubscript{2}Ag\textsubscript{3}In\textsubscript{3}Cl\textsubscript{24} \rightarrow 8 \text{CsCl} + 3 \text{AgCl} + 3 \text{InCl}_3 + 2 \text{MnCl}_2

Cs\textsubscript{8}Mn\textsubscript{2}Ag\textsubscript{3}In\textsubscript{3}Cl\textsubscript{24} \rightarrow 2 \text{CsMnCl}_3 + \frac{3}{2} \text{Cs}_3\text{In}_2\text{Cl}_9 + 3 \text{AgCl} + \frac{3}{2} \text{CsCl}

(29) \text{Cs}_2\text{Co}_{0.50}\text{Ag}_{0.75}\text{In}_{0.75}\text{Cl}_6

Cs\textsubscript{8}Co\textsubscript{2}Ag\textsubscript{3}In\textsubscript{3}Cl\textsubscript{24} \rightarrow 8 \text{CsCl} + 3 \text{AgCl} + 3 \text{InCl}_3 + 2 \text{CoCl}_2

Cs\textsubscript{8}Co\textsubscript{2}Ag\textsubscript{3}In\textsubscript{3}Cl\textsubscript{24} \rightarrow 2 \text{CsCoCl}_3 + \frac{3}{2} \text{Cs}_3\text{In}_2\text{Cl}_9 + 3 \text{AgCl} + \frac{3}{2} \text{CsCl}
(30) \( \text{Cs}_2\text{Ni}_{0.50}\text{Ag}_{0.75}\text{In}_{0.75}\text{Cl}_6 \)

\[ \text{Cs}_8\text{Ni}_2\text{Ag}_3\text{In}_3\text{Cl}_{24} \rightarrow 8 \text{CsCl} + 3 \text{AgCl} + 3 \text{InCl}_3 + 2 \text{NiCl}_2 \]

\[ \text{Cs}_8\text{Ni}_2\text{Ag}_3\text{In}_3\text{Cl}_{24} \rightarrow 2 \text{CsNiCl}_3 + \frac{3}{2} \text{Cs}_3\text{In}_2\text{Cl}_9 + 3 \text{AgCl} + \frac{3}{2} \text{CsCl} \]

(31) \( \text{Cs}_2\text{Cu}_{0.50}\text{Ag}_{0.75}\text{In}_{0.75}\text{Cl}_6 \)

\[ \text{Cs}_8\text{Cu}_2\text{Ag}_3\text{In}_3\text{Cl}_{24} \rightarrow 8 \text{CsCl} + 3 \text{AgCl} + 3 \text{InCl}_3 + 2 \text{CuCl}_2 \]

\[ \text{Cs}_8\text{Cu}_2\text{Ag}_3\text{In}_3\text{Cl}_{24} \rightarrow 2 \text{CsCuCl}_3 + \frac{3}{2} \text{Cs}_3\text{In}_2\text{Cl}_9 + 3 \text{AgCl} + \frac{3}{2} \text{CsCl} \]

(32) \( \text{Cs}_2\text{AgInBr}_{0.04}\text{Cl}_{5.96} \)

\[ \text{Cs}_8\text{Ag}_4\text{In}_4\text{Br}_1\text{Cl}_{23} \rightarrow 8 \text{CsCl} + 3 \text{AgCl} + \text{AgBr} + 4 \text{InCl}_3 \]

(33) \( \text{Cs}_2\text{AgInI}_{0.04}\text{Cl}_{5.96} \)

\[ \text{Cs}_8\text{Ag}_4\text{In}_4\text{I}_1\text{Cl}_{23} \rightarrow 8 \text{CsCl} + 3 \text{AgCl} + \text{AgI} + 4 \text{InCl}_3 \]
Figure S2: Atom projected partial density of states (pDOS) using HSE06 xc functional of (a) Cs$_2$AgCo$_{0.25}$In$_{0.75}$Cl$_6$ and (b) Cs$_2$AgIr$_{0.25}$In$_{0.75}$Cl$_6$. 

Figure S2: Atom projected partial density of states (pDOS) using HSE06 xc functional of (a) Cs$_2$AgCo$_{0.25}$In$_{0.75}$Cl$_6$ and (b) Cs$_2$AgIr$_{0.25}$In$_{0.75}$Cl$_6$. 

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Figure S3: Spatially average (a) imaginary \([\text{Im } (\varepsilon)]\) and (b) real \([\text{Re } (\varepsilon)]\) part of the dielectric function obtained by HSE06 for the pristine, and doped Cs\(_2\)AgInCl\(_6\).
Figure S4: Spatially average (a) imaginary [Im (ε)] and (b) real [Re (ε)] part of the dielectric function obtained by G0W0@HSE06 for the pristine, Cs2AgCo0.25In0.75Cl6, and Cs2AgIr0.25In0.75Cl6.

Figure S4: Spatially average (a) imaginary [Im (ε)] and (b) real [Re (ε)] part of the dielectric function obtained by G0W0@HSE06 for the pristine, Cs2AgCo0.25In0.75Cl6, and Cs2AgIr0.25In0.75Cl6.
Table S2: The high frequency ‘ion-clamped’ dielectric constant ($\varepsilon_{\infty}$) using \( G_0W_0@HSE06 \)

| Configurations                  | $\varepsilon_{\infty}$ |
|---------------------------------|-------------------------|
| pristine                        | 2.46                    |
| $\text{Cs}_2\text{AgGa}_{0.25}\text{In}_{0.75}\text{Cl}_6$ | 2.66                    |
| $\text{Cs}_2\text{AgCo}_{0.25}\text{In}_{0.75}\text{Cl}_6$ | 2.88                    |
| $\text{Cs}_2\text{AgIr}_{0.25}\text{In}_{0.75}\text{Cl}_6$ | 2.77                    |
| $\text{Cs}_2\text{Cu}_{0.25}\text{Ag}_{0.75}\text{InCl}_6$ | 2.71                    |
| $\text{Cs}_2\text{Au}_{0.25}\text{Ag}_{0.75}\text{InCl}_6$ | 2.77                    |
| $\text{Cs}_2\text{Zn}_{0.50}\text{Ag}_{0.75}\text{In}_{0.75}\text{Cl}_6$ | 2.66                    |
| $\text{Cs}_2\text{Mn}_{0.50}\text{Ag}_{0.75}\text{In}_{0.75}\text{Cl}_6$ | 2.61                    |
| $\text{Cs}_2\text{AgInBr}_{0.04}\text{Cl}_{5.96}$ | 2.69                    |
| $\text{Cs}_2\text{AgInI}_{0.04}\text{Cl}_{5.96}$ | 2.73                    |