Optical Excitations of Lead–free Double Perovskites by *Ab-initio* Excited–State Methods

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Abstract

We discuss the nature of the optical excitations of $Cs_2AgBiBr_6$, the archetypal compound of lead–free double–perovskites. Such quaternary material shows an indirect electronic bandgap with a broad optical absorption spectrum above 2 eV. By means of ab–initio excited-state methods we show that the first absorption peak is due to a bound direct exciton (X point of the Brillouin Zone), while the photoluminescence spectrum is explained in terms of phonon–assisted radiative recombination of indirect–bound excitons with transferred momenta along the L–X and Γ–X directions. To address the role of metal and halide atoms on the electronic and optical properties of this materials class, we investigate two additional ternary double-perovskites, i.e. $Cs_2In_2X_6$ (X=F, Br). Based on the accurate determination of the absorption coefficients and minimum gaps we estimate the spectroscopic limited maximum efficiency of solar cells based on such compounds, providing relevant information for their application in photovoltaics.

Bulk Hybrid Organic Inorganic Halide Perovskites (OIHPs) and derived systems have completely changed the scenario of modern, cheap, photovoltaics (PV),[1–7] as testified by the huge conversion efficiencies (PCEs) reached by the perovskite solar cells (PSCs) that nowadays pass 23%.[8] Despite the so high PCEs reached by PSCs based on the archetypal compound $MAPbX_3$ ($MA=CH_3NH_3{}^+$, methylammonium; X=halide) as light harvester, there remain issues mainly related to device stability and toxicity. For the former, the dimensionality reduction (3D → 2D, via the partial/total replacement of MA with longer-chain, hydrophobic, aliphatic (BA=butylammonium) or aromatic (PEA=phenethylammonium), organic cations), at the price of reduced PCEs, seems one of the best direction to follow.[9–12] The replacement of the organic moiety with other metallic ions (Cs), that actually recovers the OIHP parental compounds, i.e. $CsPbX_3$,[13] has been also investigated as possible strategy to improve the device stability. For the environmental issue, the replacement of Pb with other more eco–friendly elements[14] has been subject of intense research since the dawn of this new PV technology. The so-called double–perovskites where Pb(II) pairs are aliovalently replaced by two metals, one in the +1 and the other in the +3 oxidation state,[15] are compounds highly stabilized against oxidative phenomena (the main candidate in Pb replacement, i.e. Sn, easily oxidizes from +2 to +4, reducing the stability of the Sn-based OIHPs)[16] and non–toxic. Such replacement in OIHPs has been successfully investigated in combined theoretical/experimental works by Giustino who demonstrated stability and applicability of these double–perovskites in optoelectronics.[17] Still Giustino *et al.*[18] have successfully synthesized $Cs_2AgBiCl_6$, characterizing its optical properties by means of photoluminescence (PL) measurements and optical absorption. The same group succeeded in synthesizing and characterizing $Cs_2AgBiBr_6$ showing the stability of such compound and determining still by means of an experimental/theoretical approach the indirect gap of both bromine and chlorine compounds.[19] More recently they finally have characterized a similar class of compounds, Cs_2AgInX_6 (X=halide) and showed the tunability of their *direct* bandgap as function of the halide and demonstrated the possible formation of stable Cl/Br alloys.[20] The interest towards these double–perovskites is further motivated by the encouraging results provided by this new architecture not only in PV but also in photocatalysis. Indeed, Zhou *et al.*[21] have shown the impressive stability in moisture and temperature of $Cs_2AgBiBr_6$ nanocrystals making them extremely appealing for pollutant reduction. Many others are the double–metallic lead–free perovskite compounds, both already synthesized and fully characterized and also hypothetical and not yet investigated.[22] Nevertheless, those based on Ag, Bi, and In elements remain undoubtedly the most promising for optoelectronics. Also, it is worth stressing that even if +3 is the most abundant In oxidation state, a broad literature focusing on the +1 chemistry is similarly well–assessed.[23,24] More focusing on the perovskite class of compounds, $CsInF_3$ and $CsInCl_3$ (not investigated here) have been theoretically predicted to show bond disproportion,[25] while very recently the synthesis of the tetragonal compound, nominally $Cs_{1.17}In_{0.81}Cl_3$, has confirmed the coexistence of the two oxidation states in the same compound.[26] Two related species, $CsTlX_3$ (X = F or Cl), have been synthesized revealing an alternating pattern Tl(I) $\cdots$ Tl(III).[27] The same pattern has been observed in Au double perovskites,[28,29] where different Au–I bond lengths are clearly related with different oxidation states of gold atoms. Here, in view of their usage in devices,[21,30] we aim to provide and discuss the main opto-electronic features of $Cs_2AgBiBr_6$ comparing them with those of $Cs_2In(I)In(III)X_6$ (X=F, Br),[31] another emerging class of compounds isostructural with $Cs_2AgBiBr_6$ (both characterized by the elpasolite structure). In particular, by means of state-of-the-art parameter-free ground and excited-state calculations (for all the details see the SI section) - we compute the quasi-particle (QP) bandstructures, within the GW approach, and solve the Bethe-Salpeter equation (BSE) to obtain their optical properties. Our calculations clearly reveal the excitonic nature of the main optical peaks and –for the case of $Cs_2AgBiBr_6$– allow us to propose a new hypothesis concerning the nature of the observed photoluminescence spectrum and of the large measured Stokes Shift. Indeed, while the main current interpretation relies on the multi-phonons radiative recombination processes of free-carriers, we show here that the position of the PL emission and the measured Stokes Shift are fully compatible with the presence of direct and indirect bound excitons. Finally, from the accurate determination of the electronic and optical properties we calculate the maximum theoretical photo-conversion efficiency by using the SLME metrics[32] and compare the obtained values with those calculated for other two perovskites of strong interest in PV applications: MAPI and $Cs_2Au_2I_6$(see the SI for more details).

Figure 1 shows the optimized structure of $Cs_2AgBiBr_6$ discussed along the whole paper, as said $Cs_2In_2X_6$ (X=F,Br) adopts very similar structure of cubic double–perovskite (elpasolite). In $Cs_2AgBiBr_6$ the optimized lattice parameter of the primitive cell is a=7.99 Å, while those of $Cs_2In_2Br_6$ and $Cs_2In_2F_6$ are 8.12 and 6.69 Å, respectively, results which are in good agreement with those in literature.[19,33–35] In particular, for $Cs_2AgBiBr_6$ our result perfectly matches with the experimentally reported lattice parameter which ranges between 7.92 and 7.96 Å. For the other two structures, octahedrally coordinated In(I) and In(III) atoms alternate: a shorter (longer) bond length implies a reduced (larger) oxidation state. For all the species here investigated, we have calculated the Density of States (DOS). As reported for other mixed quaternary perovskites, we here observe a different contribution of the B(I) and B(III) sites (B(I)=In(I), Ag; B(III)=In(III),Bi) to the PDOS. In particular, for Br based compounds the valence band maximum (VBM) mainly consists of the orbital mixing of halide p orbitals and s orbitals of metals in +1 oxidation state. A non-negligible contribution of metals in +3 oxidation state is anyway present. For the fluorinated compound, at variance, the VBM consists of only In(I) and F orbitals, while +3 metallic orbitals are almost absent, revealing thus a more localized nature of the VBM. On the other hand, the conduction band minimum (CBM) is formed by the overlap of Bi, Br, and Ag (in decreasing amount) orbitals in $Cs_2AgBiBr_6$, with a similar trend that holds also in the case of In–based compounds, where In(III), Br/F, and In(I) (still in decreasing amount) orbitals form this band edge. As a general behaviour we observe that the DOS of the three materials shows sharper and narrow peaks near VBM with respect to CBM. Although the calculation of the electron-phonons scattering lifetimes is beyond the scope of the present work, from the above information about the DOS, we can state that the carrier non-radiative lifetime should be shorter for holes with respect to electrons: it is well–known indeed that narrow (smooth) DOS correspond to a reduced (larger) number of carrier relaxation paths that lead to longer (shorter) carrier lifetimes.[7,36–38]

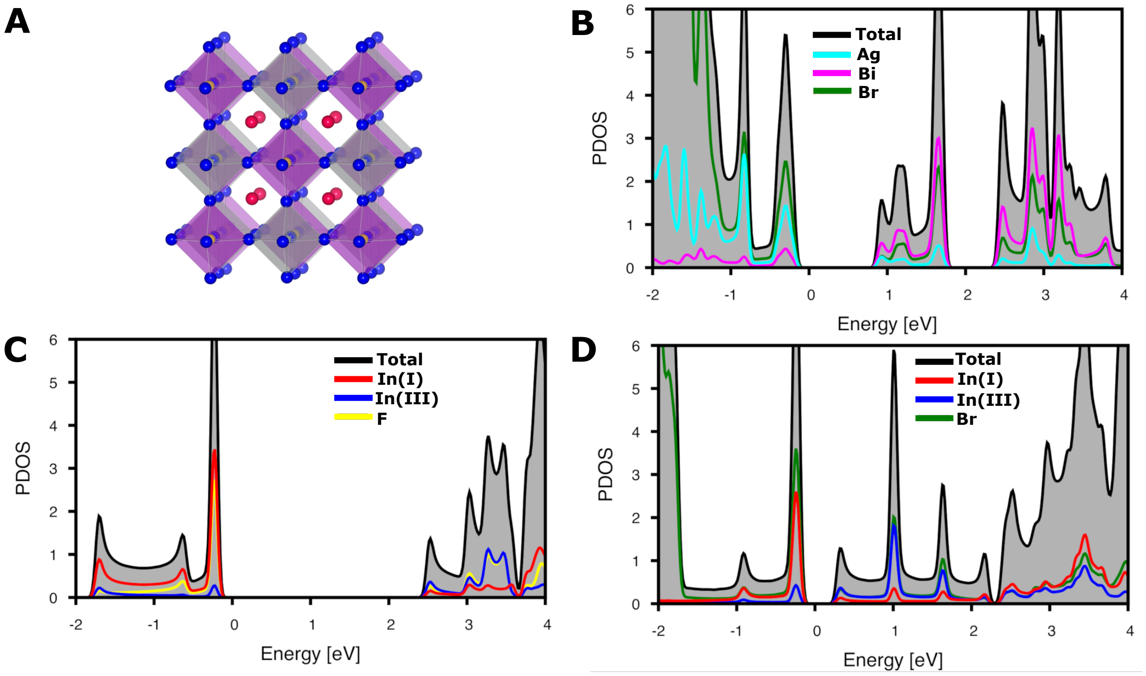

Figure 1: Panel A shows optimized structure of the $Cs_2AgBiBr_6$ crystal [red: Cs; gray: Ag; yellow: Bi; blue:Br]. DFT-PBE projected density of states of $Cs_2AgBiBr_6$ (B), $Cs_2In_2F_6$ (C) and $Cs_2In_2Br_6$ (D) including spin-orbit coupling.

The DFT-PBE bandstructures of $Cs_2AgBiBr_6$ and of $Cs_2In_2X_6$ (X=F,Br) are reported in Figure S1 of the Supporting Information section. They have been obtained without and with the inclusion of the spin-orbit interaction and our results are in essential agreement with the existing literature.[19] The corresponding quasi-particle (QP) band structures, with

SOC included, are shown in Figure 2. As expected the role of the electronic correlation beyond the DFT-KS approach is to induce a large re-normalization of the electronic gap with an opening of about 1.0 (0.7) eV for Br-based compounds and of 3.3 (3.0) eV for F-based one at GW (G_0W_0) level of approximation (Figure S2 in S.I. shows explicitly the GW convergence for the case of $Cs_2AgBiBr_6$ is reached within three iterations). The three materials present an indirect character of the minimum electronic gap which does not change moving from KS (see Figure S1 in S.I.) to QP scheme of calculation (red (blue) curves for occupied (unoccupied) states of Figure 2). The minimum indirect (direct) QP gaps are 2.1 (2.7) eV for $Cs_2AgBiBr_6$, 1.6 (2.5) eV for $Cs_2In_2Br_6$, 5.9 (6.35) eV for $Cs_2In_2F_6$. Regarding $Cs_2AgBiBr_6$, it is worth mentioning that the band structure dispersion is very similar to the one reported by Giustino *et al.*,[19] although the QP gaps, calculated here at the GW level of approximation, are about 0.3 eV larger than those calculated at the G_0W_0 level of approximation. The large value of the direct and indirect electronic gap we find here is not only in line with that obtained in ref. 19 but also in reasonable agreement with the one found at HSE06(+SOC) level of approximation in ref. 39 where a value of 3.0 eV is reported for the direct one. Nevertheless, the same authors[39] do not include excitonic effects in the calculation of the absorption spectrum obtaining an onset (similar to our IQP spectrum shown in Fig 3, see discussion below) which results at too high energy with respect to the experimental one. For the sake of completeness it is worth reporting the broad data available in literature for both direct and indirect electronic gap for $Cs_2AgBiBr_6$ at the HSE06+SOC level of calculation. Indeed for the indirect one the reported values range between 1.79 up to 2.18 eV.[40–44] More scarce is the availability of calculated direct gaps that range between 1.7 eV to 3 eV.[20,39,40]

We then move to show, in the left panel of Figure 3, the imaginary part of the dielectric function of the three double perovskites, obtained by solving the Bethe-Salpeter Equation. While $Cs_2AgBiBr_6$ has a broad spectrum (orange curve) in the VIS/UV region with the first peak around 2.3 eV, a very intense optical peak at about 2.1 eV and 5.5 eV is present for

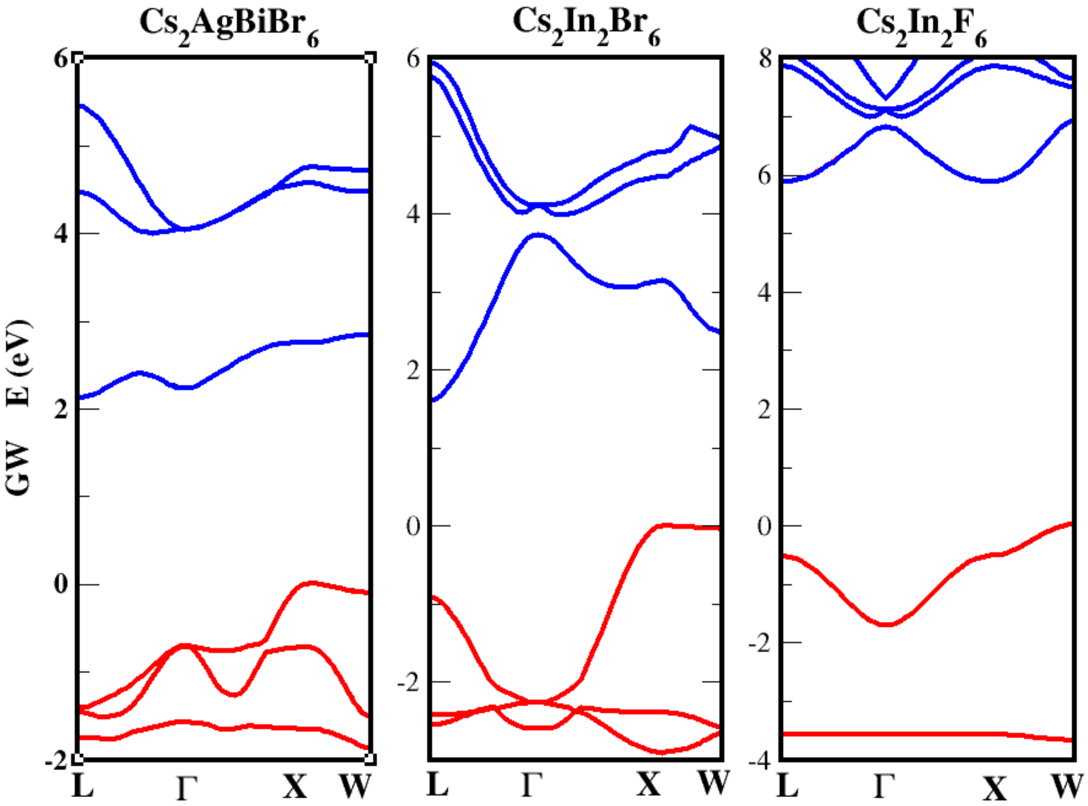

Figure 2: Quasi-particle (QP) electronic band structures obtained within the GW perturbative approach: (red (blue) indicate occupied (unoccupied)) bands. The top of the valence band has been shifted to zero energy for all the cases.

$Cs_2In_2Br_6$ (black curve) and $Cs_2In_2F_6$ (blue curve), respectively. In the same figure, for each material, the value of the QP direct (indirect) gaps are indicated by up (down) arrows. It is then straightforward to extract the exciton binding energy (E^b_{exc}) of the first bright direct exciton (corresponding to the position of the first optical absorption peak) which is 0.34, 0.35, and 0.85 eV for $Cs_2AgBiBr_6$, Cs_2InBr_6 and $Cs_2In_2F_6$, respectively. In the first case (two latter) the lowest bright exciton is built up mainly by a mixing of IQP transitions near X (W) point, among VBM to CBM. From the analysis of the BSE eigenvalues we find that several optically inactive excitons are present below the first bright one, with E^b_{exc} of the lowest energetic dark exciton at 0.48, 0.44, and 1.34 eV, respectively. Regarding the large values of E^b_{exc} obtained in the present work, it is important to point out which could be the role of the ionic contribution to the dielectric screening. Indeed, this is often considered as one of the main sources of the small excitonic binding energy in hybrid halide perovskites (see i.e. Refs 45–47). In a recent work[48] Kresse and coworkers have shown (for $\mathrm{MAPbI_3}$ and other hybrid halide perovskites) that when the exciton binding energy is much larger than the energy of the Longitudinal Optical (LO) phonon mode, there is a negligible ionic contribution to the effective dielectric screening determining E^b_{exc}, which is then not lowered by ionic screening. Following a similar argument, being here $E^b_{exc} >> \hbar\omega_{LO}$ (see the phonons DOS reported in Figure S3 in S.I.), we can exclude, at least in ideal double perovskites with ordered atomic structures, that the ionic contribution plays a role in the exciton binding energy values. The right panel of Figure 3 illustrates the good comparison between the theoretical BSE (full orange curve) and the experimental spectrum (black data, taken from ref. 33) of $\mathrm{Cs_2AgBiBr_6}$. The corresponding theoretical spectrum calculated at independent quasi-particle (IQP) level of approximation (orange dashed curve) is also reported to highlight again the importance of the inclusion of excitonic effects for a comparison with experimental data. It is worth mentioning that a similar good agreement is also found with experimental data reported in Refs. 49,50, which show a sharp decrease at about 2.7-2.8 eV, feature present also in our BSE absorption curve. As mentioned before, $\mathrm{Cs_2AgBiBr_6}$ is characterized by a broad PL spectrum below 2 eV whose origin is still under debate: while several authors connect it to multiple phonon-assisted radiative inter-band recombination,[33,49] others relate it to the presence of spatially localized color centers.[50] Although *ab-initio* calculations of phonon-assisted PL spectra start to be available in the literature by means of non-equilibrium Greens functions plus finite-difference electron-phonon coupling,[51,52] here it would be prohibitive from a computational point of view due to the large unit cell. We focus then, on the energy loss function $\Gamma(\mathbf{q},\omega) \propto Im(\frac{1}{\epsilon}(\mathbf{q},\omega))$ calculated at the $\mathbf{q}$ vectors of interest ($\mathbf{q} = L - X, \Gamma - X$, red and magenta curves in Fig. 3) and including the e-h interaction. This calculation can provide a clear evidence of the presence of indirect bound excitons, allowing to verify if their energy is in the same range of the observed PL emission. Indeed, assuming as the most probable process that one involving a single LO phonon and if this mode has a very small energy (as in the present case,[53] see also SI) the PL spectrum should have the onset at the same energy of the lowest indirect excitons. Notably, the EELS spectra (red and magenta curves) show peaks below 2 eV, in the same energetic region of the observed PL (shaded yellow rectangle). This provides a strong indication of the fact that the PL is due to phonon-assisted radiative recombination of indirect bound excitons with $\mathbf{q} = L - X, \Gamma - X$ and energies 1.8, and 1.9 eV, respectively. From our analysis we can conclude that the large measured Stokes shift is compatible with the energy difference between the direct and the indirect excitonic interband transitions. This result can in some way reconcile the inconsistency between the large Huang-Rhys factor S extracted from the measured Stokes shift and the not too large values of the Frölich constants $\alpha_e = 2.54$ and $\alpha_h = 2$ calculated recently by Steele *et al.*[49] Furthermore the idea that bound excitons are at the origin of the observed PL, is also compatible with the presence of spatially localized (see the discussion of Figure 4) states below the electronic gap, which have been experimentally identified in Ref. 50 but interpreted there as color centers. Finally starting from the QP energies, the values of the Frölich constants reported above and the energy of the longitudinal optical mode, we estimate the energy shift due to the formation of large polarons from the mesoscopic Fröhlich model, in a similar way to what was done in Ref. 48, obtaining a reduction of the QP gap of about 0.09 eV. This means that, although the polaronic state is less stable than the indirect bound excitons, part of the photo-excited direct excitons can decay there and then rapidly separate in space, never reaching the lowest indirect exciton bound state. Furthermore, charge separation after optical excitation can be favoured by non-regularities in the electrostatic potential not taken into account in our simulations but realistically occurring in experimental samples. We are clearly aware that the role of atomic disorder, scattering, impurities, and multi-phonon processes cannot be discarded, but the present analysis shows that the excitonic nature of the optical properties plays a crucial role for a correct interpretation of the experimental data. To further characterize the excitonic properties of the three double perovskites, we show in

Figure 4 the wavefunction modulus square of the first bright direct exciton.

For $Cs_2In_2F_6$ (right panel) fixing the hole near an F atom (black triangle), the electron localizes mainly near the first neighbour In atoms, as shown by the green isosurface (corresponding to 15 %), showing a very strong spatial localization. An increase of the excitonic spatial delocalization is instead visible in the two plots of $Cs_2AgBiBr_6$ and $Cs_2In_2Br_6$, where the electron prefers to be near In sites when the hole position is fixed near an halogen atom (black triangle).

Due to the large absorption coefficients and gap in the visible region, $Cs_2AgBiBr_6$ is a material of interest for possible PV applications and similarly it should apply to $Cs_2In_2Br_6$. We then calculated the Spectroscopic Limited Maximum Efficiency (SLME)[54] that has been proved to be a good metrics to determine the maximum efficiency that an absorber material can reach in a single-junction solar cell. It has been derived by Yu and Zunger[32] within the thermodynamic detailed balance, but differently from the Shockley and Queisser (SQ) limit,[55] it considers the existence of various energetic sequences of direct (dipole allowed and forbidden) and indirect band gaps, the specific shape of the absorption near the threshold, and the dependence of non-radiative recombination losses on the energy separation between the minimum and the direct gap. The SLME calculation requires as input the standard solar spectrum, the absorption coefficient of the material and also the values of the direct and indirect electronic gaps. The calculated SLME curves are almost constant for thickness larger than $1\mu m$ reaching the values reported in Table 1.

Table 1: Calculated Spectroscopic Limited Maximum Efficiency (SLME) for the three double perovskites. Values are compared with those obtained for MAPI and for $Cs_2Au(I)Au(III)I_6$

Material	SLME (%)
$Cs_2AgBiBr_6$	10.5
$Cs_2In_2Br_6$	11.5
$Cs_2In_2F_6$	0.1
MAPI	26
$Cs_2Au_2I_6$	30

Our theoretically predicted $Cs_2AgBiBr_6$ SLME is in good agreement with previous theoretical reported one (7.92 %@HSE06+SOC).[40] Comparing our value with experimentally reported PCEs for $Cs_2AgBiBr_6$ which are in the order of $\sim 3\%$,[56–58] we predict large room for experimentally improving the light harvesting performances for the two bromine based materials. Anyway, in single–junction solar cells based on ordered defect–free materials, the efficiency is likely not to reach the large values obtained by current OIHPs based devices. In this sense our predicted SLME for MAPI (26.0%) is in good agreement with previous theory (24.94 % @HSE06+SOC),[59] slightly larger, as expected, than the experimentally reported PCE values of 25.2%.[8] The value predicted for the $Cs_2Au_2I_6$ which is another Pb-free perovksite receiving increasing attention recently, confirms the high potential of this material for PV application as suggested recently by Debicchi et al.[29] Finally for $Cs_2In_2F_6$, due to the larger gap in the UV region, the calculated SLME is clearly very small.

In conclusion, by means of ground and excited-state *ab-initio* simulations, we have here discussed and compared structural, electronic, and optical features of two classes of Pb–free double–perovskites, i.e. stoichiometrically quaternary $Cs_2AgBiBr_6$ and ternary $Cs_2In_2X_6$ (X=F,Br). For the former, in particular, we observe that its first absorption peak is the result of a bound exciton close to the X point, while the photoluminescence spectrum is a phonon–assisted radiative recombination process of indirect bound excitons. Importantly, using our theoretical absorption coefficients and direct/indirect bandgaps we have calculated the Spectroscopic Limited Maximum Efficiency of these materials and observed a large room for enhancing their conversion efficiencies as light harvesters in devices.

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXX.

Theoretical details of DFT, *GW*, BSE, and Spectroscopic Limited Maximum Efficiency calculations are reported. Additional theoretical results are shown and include the electronic band structure of $Cs_2AgBiBr_6$, $Cs_2In_2Br_6$, and $Cs_2In_2F_6$ (with and without spin-orbit coupling inclusion), total phonon density of states of the three species, convergence test of quasiparticles energies (calculated at G_0W_0, G_1W_1, and G_3W_3) vs. Kohn-Sham ones for $Cs_2AgBiBr_6$, and the optical spectra (BSE+G_0W_0) for the three species calculated (as convergence test) with 4×4×4 and 6×6×6 *k*-grids at G_0W_0 level and using a rigid scissor for both and using 4 occupied and 4 unoccupied states.

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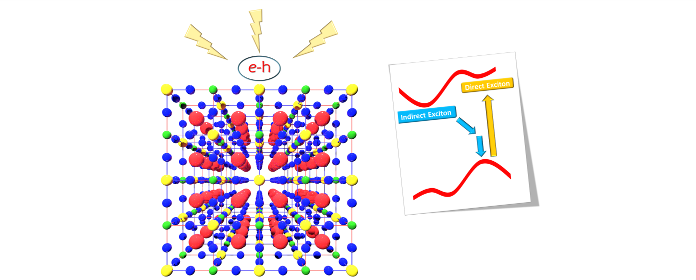
Graphical TOC Entry



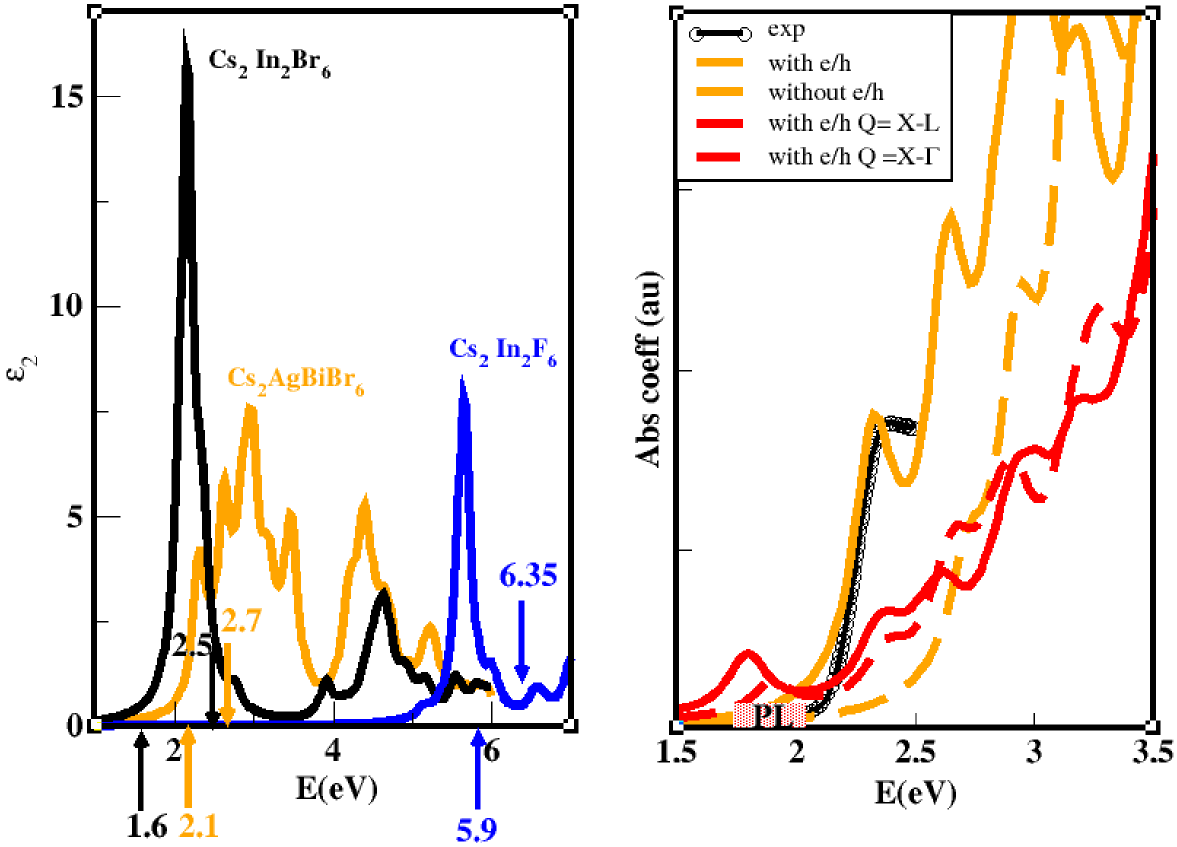


Figure 3: Left panel: imaginary part of the dielectric function for the three double-perovskites, obtained taking into account the QP corrections calculated at the *GW* level of approximation and also including the excitonic and local-field effects through the solution of the Bethe-Salpeter equation. The up-oriented (down) arrows (and relative numbers) indicate the energetic positions of the indirect (direct) minimum quasi-particle gap. Right panel: Theoretical Absorption coefficient with (orange solid curve) and without (orange dashed curve) the local field and excitonic effects, compared with the experimental curve (black curve) from ref.[33] The magenta and red solid curves are the EELS spectra calculated. with e-h effects included, for finite transferred momentum **Q** corresponding to the lowest indirect transition **L** - **X** and Γ - **X** respectively. The energetic region where the PL is observed, is indicated schematically by the shaded yellow area.

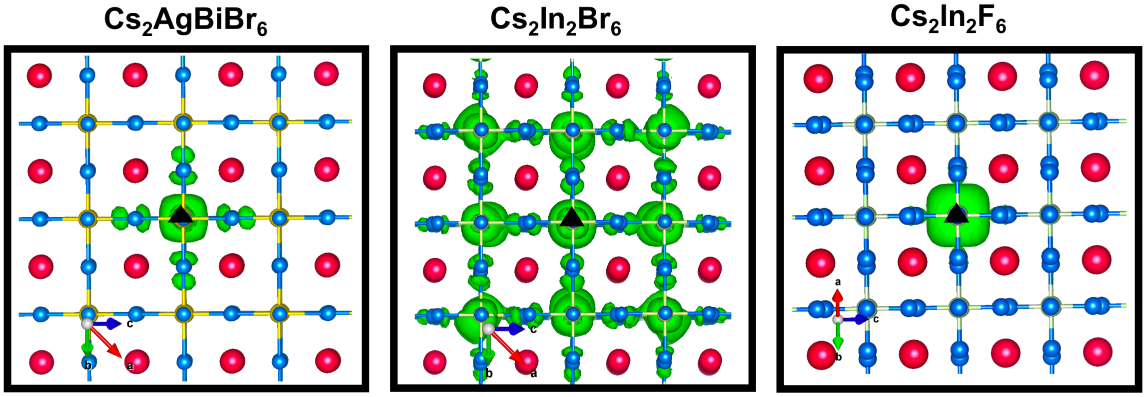

$Cs_2AgBiBr_6$ $Cs_2In_2Br_6$ $Cs_2In_2F_6$

Figure 4: The green isosurface (15% of the maximum value) represents the probability to find the electron when the hole is fixed in given probable position (here shown as the black triangle). F atoms are blue dots, Br (pale blue) Cs (red) In(pale yellow), Ag (pale green) Bi (yellow)