Band Gap Tuning Through Cation and Halide Alloying in Mechanochemical Synthesized Cs$_3$(Sb$_{1-x}$Bi$_x$)$_2$Br$_9$ and Cs$_3$Sb$_2$(I$_{1-x}$Br$_x$)$_9$ Solid Solutions

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ABSTRACT

Modulation of optical properties of lead-free defective perovskites can contribute to design optimized materials for several applications ranging from photodetection to photocatalysis. Here, we explored two novel alloying strategies on Cs$_3$Sb$_2$Br$_9$, by preparing by mechanochemical synthesis Sb/Bi and Br/I mixed systems. An unexpected band gap bowing has been observed in alloyed Sb/Bi compositions, showing lower absorption edges with respect to pure compounds. Such behavior has been computationally modelled suggesting the presence of local aggregates as the source of such reduction of the band gap. Further modulation of the optical properties has been achieved by halide alloying showing a progressive red-shift by increasing the iodide content. In both cases a full solubility at the solid state has been determined by means of diffraction and Raman spectroscopy. Overall, this study proposes and rationalizes doping strategies in the Cs$_3$Sb$_2$Br$_9$ defective perovskite achieved through the use of a sustainable synthetic procedure such as mechanochemistry.

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Introduction

In the last decade, metal-halide perovskites (MHPs) have grown to the most promising material classes for future photovoltaic (PV) devices. While their huge potential is out of question, recent experimental and computational research expands beyond the class of lead-halide perovskites exploring chemical and structural phase spaces of MHPs and perovskites derivatives.\textsuperscript{1} Several structural diverse systems are now under investigation, including, for example, 3D, 2D, and double perovskites, targeting applications beyond PV, as \textit{e.g.} photodetection and photocatalysis.\textsuperscript{2–11}

The expansion of the discovered material space of MHPs has recently moved towards the investigation of lead-free systems in order to overcome the concerns related to Pb-toxicity. While effective alternatives for PV applications rely most on tin-based compositions, several other phases containing different metals such as Bi, Sb, Cu, Ge, have been discovered and investigated.\textsuperscript{12–19} In many cases, such perovskites resulted to be not suitable for PV devices but possess very appealing optoelectronic properties which can be exploited in other applications. Among these systems, bismuth- and antimony-based perovskite derivatives of general formula $\text{Cs}_3\text{M}_2\text{X}_9$ ($\text{M}=\text{Bi, Sb}; \text{X}=\text{Br, I}$) have shown a strong technological potential in particular in the area of photocatalysis (both for solar fuel generation and organic synthesis) and photodetection.\textsuperscript{20–36}

Bismuth-based defect-ordered perovskites have been object of more intense studies with respect to the corresponding Sb systems, notwithstanding their appealing optoelectronic properties such as high carrier mobility, low trap density, and long diffusion length. As a matter of fact, $\text{Cs}_3\text{Sb}_2\text{Br}_9$ millimeter-sized single crystals and nanoflakes have been applied in the fabrication of photodetectors with excellent performance in terms of responsivity and detectivity.\textsuperscript{37,38} Good photodetectors based on $\text{Cs}_3\text{Sb}_2\text{Br}_9$ have been also prepared by means of chemical vapor deposition technique.\textsuperscript{39} $\text{Cs}_3\text{Sb}_2\text{I}_9$ and $\text{Cs}_3\text{Sb}_2\text{I}_9$ revealed also to be suitable
candidates for photocatalytic applications and in this respect have been, for example, applied in the photocatalytic carbon dioxide reduction, water splitting, and in aromatic C-H bond activation.\textsuperscript{40–44} Some efforts has been also applied in the possible use of these defect-ordered perovskites in the manufacturing of solar cells. Cs$_3$Sb$_2$I$_9$ has been preferentially used in for PV due to its suitable band gap around 2 eV, providing good stability but relatively low efficiencies around 2-3\%.\textsuperscript{45–47}

While there is a clear relevant interest in Sb-based materials, many of their fundamental features still need to be explored, for example, in terms of synthetic procedures, band gap tuning by metal or halide alloying, and their electronic structure. Considering the structural and optoelectronic similarity with Bi-based analogues, which have been more deeply investigated, it appears that some tuning strategies of the photophysical properties of Sb materials should be clarified to enlarge the plethora of lead-free perovskite derivatives. For example, the preparation of mixed Sb/Bi phases of vacancy ordered perovskites has not been reported in the current literature but there is a strong motivation to investigate such a system. Indeed, a recent work on the Cs$_2$Ag(Sb$_x$Bi$_{1-x}$)Br$_6$ double perovskite solid solution has demonstrated a nonlinear trend of the band gap value as a function of $x$, providing mixed compositions with lower values with respect to Cs$_2$AgBiBr$_6$ and Cs$_2$AgSbBr$_6$.\textsuperscript{48} However, the possibility of successfully preparing a continuous solid solution within the vacancy-ordered Cs$_3$(Sb$_{1-x}$Bi$_x$)$_2$Br$_9$ system has still to be verified. The choice of a suitable synthetic route for these Sb/Bi materials is critical due to the low solubility of halide precursors posing strong limitations for traditional synthesis procedures applied to MHPs. A viable choice could be the use of mechanochemistry which has been recently applied to Bi-based systems but never to Sb-containing perovskites or mixed compositions. Finally, the halide alloying strategy to modulate the optical properties of perovskites has still to be investigated in Sb vacancy-ordered materials.

Based on the above considerations, in this work we carried out the mechanochemical synthesis of the Cs$_3$(Sb$_{1-x}$Bi$_x$)$_2$Br$_9$ and Cs$_3$Sb$_2$(I$_{1-x}$Br$_x$)$_9$ systems ($0 \leq x \leq 1$) to understand the role
of Sb/Bi and I/Br alloying on the structural and optical properties. For both alloying routes, we employ mechanochemistry as the main preparation technique to verify its suitability to Sb-based systems and its ability in providing phase-pure mixed compositions.
RESULTS AND DISCUSSION

\textit{Cs}_3(Sb_{1-x}Bi_x)_{2}Br_9 System

Powdered samples of the \textit{Cs}_3(Sb_{1-x}Bi_x)_{2}Br_9 system for \(x=0, 0.1, 0.2, 0.4, 0.6, 0.8, 0.9, \) and 1 have been prepared by using a planetary ball miller according to the experimental conditions reported in the Experimental Section (see the Supporting Information, SI). Figure 1 shows the appearance of the eight samples prepared from \textit{Cs}_3Sb_{2}Br_9 (left) to \textit{Cs}_3Bi_{2}Br_9 (right).

![Figure 1](image)

\textbf{Figure 1}. Photograph reporting the samples of \textit{Cs}_3(Sb_{1-x}Bi_x)_{2}Br_9 solid solution.

Figure 2 reports the room temperature (RT) x-ray diffraction (XRD) patterns collected on all the samples reported in Figure 1. Samples have been measured both with Cu-K radiation (Figure 1) and with Mo-K radiation (Figure S1) to provide the most reliable structural results on these novel samples. Compositions (expressed as \(x\)) in Figure 1 refer to the effective stoichiometries determined by microprobe analysis (see later in the text). All the samples are single phase and are in agreement with the hexagonal symmetry of the \textit{P}-3\textit{m}1 space group describing the two end members, namely \textit{Cs}_3Sb_{2}Br_9 and \textit{Cs}_3Bi_{2}Br_9. A superposition of the reference structure model for these last two samples and the experimental patterns are shown in Figures 2b and 2c, respectively.
Figure 2. (a) XRD patterns of a $\text{Cs}_3(\text{Sb}_{1-x}\text{Bi}_x)\text{Br}_9$ solid solution as a function of $x$; b) diffraction pattern of $\text{Cs}_3\text{Bi}_2\text{Br}_9$ superimposed to the calculated pattern of the hexagonal structure (vertical red lines); c) diffraction pattern of $\text{Cs}_3\text{Sb}_2\text{Br}_9$ superimposed to the calculated pattern of the hexagonal structure (vertical blue lines).

According to these results, the mechanochemical synthetic procedure was effective in preparing single-phase materials for both the two stoichiometric compositions $\text{Cs}_3\text{Sb}_2\text{Br}_9$ and $\text{Cs}_3\text{Bi}_2\text{Br}_9$, and for the mixed Sb/Bi samples. Such green and sustainable synthetic approach has never been applied to Sb-based defective perovskites nor to B-site mixed compositions, while
a previous report on its effective use for the preparation of $\text{Cs}_3\text{Bi}_2\text{Br}_9$ is reported in the current literature.\textsuperscript{49}

The morphology and chemical composition of the samples has been determined by means of scanning electron microscopy (SEM) and microprobe analysis. Images of the sample morphology are reported in Figure S2. As a consequence of the mechanochemical synthesis, the samples do not possess a well-defined morphology, as occurs in solution chemistry synthesis, and grains with various shapes and dimensions (in the micron and sub-micron range) are observed. Elemental analysis by SEM confirmed a good agreement with the nominal compositions (see Table 1). In the rest of the paper, we will make use of the effective compositions instead of the nominal ones when discussing the experimental results.

The XRD patterns have been refined by Rietveld method. The lattice parameters determined are reported in Table 1, while Figures 3a-c show their trend together with lattice volume as a function of $x$ (Bi-content).

Table 1. Composition determined by microprobe analysis, lattice parameters and band gap (BG) values for the $\text{Cs}_3(\text{Sb}_{1-x}\text{Bi}_x)_2\text{Br}_9$ samples.

<table>
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<tr>
<th>Nominal ($x$)</th>
<th>Effective ($x$)</th>
<th>$a=b$ (Å)</th>
<th>$c$ (Å)</th>
<th>Volume (Å$^3$)</th>
<th>Direct BG (eV)</th>
<th>Indirect BG (eV)</th>
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<td>9.8422(4)</td>
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<td>2.58</td>
<td>2.46</td>
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</table>
Figure 3. Trend of (a) $a=b$ lattice parameter, (b) $c$ lattice parameter, and (c) cell volume for the samples of the $\text{Cs}_3(\text{Sb}_{1-x}\text{Bi}_x)\text{Br}_9$ solid solution as a function of $x$.

The linear trend of the lattice volume reported in Figure 3c agrees with the Vegard’s law for solid solution, confirming the complete solubility of Sb/Bi in the lattice. This result could be anticipated based on the similar ionic radii between $\text{Sb}^{3+}$ and $\text{Bi}^{3+}$ ions and the same crystal structure of the two end-members.

The Raman investigation has been performed focusing on the low energy part of the Raman activity, i.e. in the range 25-250 cm$^{-1}$. At a first glance, the single-phase of the endmembers’ samples is confirmed, as reported in Figure 4a. Indeed, the Raman spectrum of
the Cs$_3$Bi$_2$Br$_9$ sample clearly shows the characteristic modes at 165 and 190 cm$^{-1}$, due to the bond vibrations inside the octahedral cage, BiBr$_6$, as already described in our previous work.$^{36}$

In analogy with the isomorphic Cs$_3$Bi$_2$Br$_9$, also for Cs$_3$Sb$_2$Br$_9$ the Raman response qualitatively presents the same spectral fingerprints: a broadened structure centered at about 70 cm$^{-1}$ clearly resulting from the overlapping of different modes and two sharp and symmetric modes peaked at 182 and 210 cm$^{-1}$, resulting from the Sb-Br bond vibrations in the octahedral unit SbBr$_6$. The proper assignment of the mode symmetry seems to be controversial.

Figure 4. a) Comparison between room temperature (RT) Raman spectra of the endmembers. b) Color map reporting the modes intensity of the samples’ spectra in the range between 150 and 225 cm$^{-1}$ as a function of the Bi content (we applied a power-law normalization to remap the colors, to increase the contrast and better point out the change in the mode position).

Indeed, in ref. 50, the mode at 210 cm$^{-1}$ is given an A$_{1g}$ symmetry and the one at 182 cm$^{-1}$ an E$_{1g}$ one, while in ref. 37, the opposite.$^{37,50}$ However, besides this discrepancy, the two vibrational modes foreseen the displacement of both Sb and Br atoms, as it is for the Cs$_3$Bi$_2$Br$_9$ sample.$^{50}$ The Raman spectra for the whole set of samples moving from Cs$_3$Bi$_2$Br$_9$ to Cs$_3$Sb$_2$Br$_9$ in the region between 25 and 280 cm$^{-1}$ are reported in Figure S3. It is clear that the progressive substitution of the Sb atoms with the heavier Bi ones highly affects the modes above 150 cm$^{-1}$.

From these data we derived a color map (Figure 4b) showing the energy changes experienced
by the $A_{1g}$ and $E_g$ modes by gradually varying the relative abundance of Sb and Bi. The energy changes of the main Raman bands indicate a clear two-mode behavior, where for small amount of Bi, the modes proper of the Cs$_3$Bi$_2$Br$_9$ sample already affect the collected spectra with a constant increase of their intensities as the number of BiBr$_{6}$ units progressively replace the SbBr$_{6}$ ones. The increasing Br amount causes a redshift of the Raman bands, particularly pronounced for the mode at 210 cm$^{-1}$, according to a progressive cell expansion with a consequent increase of the interatomic distance, as pointed out by the XRD measurements, the Br substitution caused.

The crossover between Bi-rich to Sb-rich system is also well evidenced in Figure S4a where the intensity of the mode at about 165 cm$^{-1}$ proper of Cs$_3$Bi$_2$Br$_9$ and the one at 210 cm$^{-1}$ of Cs$_3$Sb$_2$Br$_9$ are plotted as a function of the Bi content: as the former increases, the latest decreases. In Figure S4b, the spectrum for the $x = 0.57$ sample is reported together with the result from the best-fitting procedure using four Lorentzian curves according to the above mentioned two-mode behavior.

Figures 5a reports the UV-Vis reflectance spectra collected on the whole series of samples of the Cs$_3$(Sb$_{1-x}$Bi$_x$)$_2$Br$_9$ solid solution. It can be seen that the absorption edges of the two stoichiometric compounds, i.e. the red spectrum for Cs$_3$Sb$_2$Br$_9$ and the blue spectrum for Cs$_3$Bi$_2$Br$_9$, are blue-shifted with respect to all the mixed compositions. Bi-and Sb-based defective perovskites present a dual direct-indirect transition which has been previously observed and described also from a computational point of view.$^{51,52}$ The values of the direct and indirect band gaps determined from the Tauc plots (reported in Figure S5) are shown in Figure 5b as a function of $x$. 
Figure 5. (a) absorption spectra and (b) trend of the band gaps of the Cs$_3$(Sb$_{1-x}$Bi$_x$)$_2$Br$_9$ solid solution.

The values of direct and indirect band gaps for Cs$_3$Sb$_2$Br$_9$ and Cs$_3$Bi$_2$Br$_9$ are in agreement with those previously reported in the current literature.\textsuperscript{34,36,39,51} By looking at Figure 5b, a significant bowing of the band gap for mixed compositions is observed. This result is unexpected since, in general, metal ion replacement in solid solution provides a scaling of the band gap obeying the Vegard’s law. The reduction of the band gap (direct) for mixed compositions is relevant, reaching a minimum value of about 2.35 eV when $x$ is around 0.2. The same trend in the band gap bowing is observed for the indirect band gap. Such a trend has never been observed before in any defective perovskite but has been reported for the double perovskite system Cs$_2$AgSb$_{(1-x)}$Bi$_x$Br$_6$ and attributed to chemical rather than structural effects.\textsuperscript{48} In our case we cannot exclude a synergistic effect due to coexistence of mass disorder and microscopic strain as expected in a two-mode scenario evidenced by Raman data.\textsuperscript{48} The present results corroborate the strategy of band gap tuning by Sb/Bi mixing which seems to be general considering the structural difference between defective perovskite and double perovskites and therefore related to the peculiar electronic properties of antimony and bismuth in mixed compositions.
To understand the unexpected change in the band gap, density functional theory (DFT) calculations have been performed for the reference systems Cs$_3$Sb$_2$Br$_9$ and Cs$_3$Bi$_2$Br$_9$ as well as the mixed Cs$_3$(Sb$_{0.5}$Bi$_{0.5}$)$_2$Br$_9$. Ionic positions of the three systems were obtained by PBE+D3 geometry optimization, followed by refined electronic structure calculations using the hybrid HSE06 functional including spin–orbit coupling (see SI for computational details). The indirect bandgap and first direct transition of Cs$_3$Bi$_2$Br$_9$ (Cs$_3$Sb$_2$Br$_9$) were calculated to be 2.97 (2.91) and 3.10 (2.96) eV, respectively (see Table 2). Previous GW-BSE calculations showed large exciton binding energies of ~300 meV, which are not captured in our DFT calculations. Correcting our DFT results by the large exciton binding energies results in a fair agreement with the experimental band gap values.

<table>
<thead>
<tr>
<th></th>
<th>Cs$_3$Sb$_2$Br$_9$</th>
<th>Cs$<em>3$(Sb$</em>{0.5}$Bi$_{0.5}$)$_2$Br$_9$</th>
<th>Cs$_3$Bi$_2$Br$_9$</th>
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<tbody>
<tr>
<td>D/I</td>
<td>i</td>
<td>I</td>
<td>i</td>
</tr>
<tr>
<td>BG Direct</td>
<td>2.96</td>
<td>2.71</td>
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</tr>
<tr>
<td>BG Indirect</td>
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</tr>
<tr>
<td>Exp. Direct</td>
<td>2.50</td>
<td>2.34</td>
<td>2.58</td>
</tr>
<tr>
<td>Exp. Indirect</td>
<td>2.31</td>
<td>2.11</td>
<td>2.46</td>
</tr>
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</table>

Table 2. Theoretical and experimental values of the direct and indirect band gap energies for the pure Cs$_3$Sb$_2$Br$_9$ and Cs$_3$Bi$_2$Br$_9$ compounds and for the mixed Cs$_3$(Sb$_{0.5}$Bi$_{0.5}$)$_2$Br$_9$. All theoretical values are on the HSE06+SOC level of theory, neglecting excitonic effects on the absorption energies which are of ~300 meV.

For the pure Sb and Bi species, the contribution of valence band is primarily given from bromine 4p orbitals with slight metal contribution, while the conduction band is mainly due to the metal cation (for Sb 5p orbitals and Bi 6p orbitals) and its interaction with bromine 4p orbitals, see Figure 6a. Moving to the mixed Bi/Sb material, we observe substantial differences depending on the arrangement of the metal ions. The fully mixed system, with alternating SbBr$_6$
and BiBr$_6$ octahedra, interestingly shows a negligible difference in band gaps, with indirect and direct bandgap of 2.90 and 3.00 eV, compared to the pure Sb and Bi species, see Figure S6. When we consider aggregates of Sb and Bi, see Figure 6b, we observe a decrease to 2.59 and 2.71 eV of the indirect and direct band gaps, respectively, see Figure 6a. In terms of stability, the two models show the same energy suggesting that both appear equally in the crystal structure. This clearly suggests that the decreasing of the band gap experimentally found for the mixed Sb/Bi material is associated to the presence of this kind of aggregates. In fact, considering the energy alignment in the density of states, Figure 6a, we find an upshift of the VB and CB moving from Cs$_3$Bi$_2$Br$_9$ to Cs$_3$SbBiBr$_9$ of 0.52 eV and of 0.15 eV, respectively. In contrast, the VB is nicely aligned with the Cs$_3$Bi$_2$Br$_9$ compound, showing a shift of only 0.21 eV, compared to a large CB shift of 0.53 eV. The DOS of the mixed Cs$_3$SbBiBr$_9$ shows that the VB is mainly associated to the Br with a slight Sb contribution, while the CB is made up of the Bi and Br states in similar ratio. Consequently, we can explain the drop in the band gap upon Sb/Bi alloying by the formation of SbBr$_6$ and BiBr$_6$ aggregates, which dominate the VB and the CB, respectively, as schematically shown in Figure 6c. This is the first report of such an effect in this Sb/Bi vacancy ordered perovskite alloys, while an analogous trend was found for the double perovskite system Cs$_2$AgSb$_x$Bi$_{(1-x)}$Br$_6$.\textsuperscript{48}
Figure 6. (a) Calculated DOS for (top) Cs$_3$Sb$_2$Br$_9$, (middle) Cs$_3$SbBiBr$_9$, and (bottom) Cs$_3$Bi$_2$Br$_9$. All DOS are aligned with respect to the valence band maximum of Cs$_3$Bi$_2$Br$_9$. (b) Structural representation of the mixed Cs$_3$SbBiBr$_9$ system, showing aggregation of Sb- and Bi-centered octahedra. SbBr$_6$ and BiBr$_6$ octahedra are visualized by red and pink polyhedra, respectively. Cs atoms are shown in green. For simplicity, Br atoms are removed from the visualization. (c) Schematics of the band contributions upon mixing in Cs$_3$(Sb$_{1-x}$Bi$_x$)$_2$Br$_9$: Conduction band edge is dominated by the Bi aggregates, while the valence band edge is dominated by the Sb aggregates.

The band gap bowing of mixed metal perovskites has been observed in Pb/Sn perovskites and attributed to chemical effects mismatch in energy between s and p atomic orbitals of the two metals. A similar interpretation holds also the present Cs$_3$(Sb$_{1-x}$Bi$_x$)$_2$Br$_9$
solid solution where a mismatch in energy between s and p atomic orbitals of Sb and Bi is found. It is of relevance to report here this novel tuning strategy for defective perovskites which allows to achieve significant lower band gap values through metal alloying instead of the usual halide mixing which is known to be the main strategy to modulate the absorption edge in these systems.\textsuperscript{25,26,36}

\textit{Cs}_3\textit{Sb}_2(\textit{Br}_{1-x}\textit{I}_x)_9 System

We further explored alloying strategies by tuning the halide content Br/I on the \textit{Cs}_3\textit{Sb}_2\textit{Br}_9 perovskite. While such strategy has been explored for the Bi analogue, no studies are reported for the Sb-based composition.\textsuperscript{25,36} For this purpose, samples of the \textit{Cs}_3\textit{Sb}_2\textit{Br}_{9-x}\textit{I}_x system for \(x=0\) (also reported above), 2.5, 4.5, 6.5, and 9 have been synthesized by means of mechanochemistry according to the experimental conditions reported in the SI. Photographs of the five samples are reported in Figure 7a. The XRD patterns of the whole series of samples are reported in Figure 7b. For the \textit{Cs}_3\textit{Sb}_2\textit{I}_9 perovskite two different polymorphs have been reported, namely the layered modification with s.g. \(P-3m1\) (analogous to \(P3\text{\textit{m}}1\), see above) and the dimer modification with space group \(P6_3\text{\textit{mmc}}\), featuring SbI\(_6\) octahedra fused into Sb\(_2\)I\(_9\)\(^{-3-}\) dimers through sharing of their triangular faces.\textsuperscript{55} According to literature, the dimer form is synthesized from solution using a polar solvent, whereas the layered form is obtained from a solid state reaction at low temperatures.\textsuperscript{56} However, the present synthetic approach has never reported before for \textit{Cs}_3\textit{Sb}_2\textit{I}_9 and additional information on the stability of the different polymorphs have been obtained. According to Figure 7c, reporting the XRD patterns of \textit{Cs}_3\textit{Sb}_2\textit{I}_9 perovskite against the expected structure for the \(P-3m1\) space group, we could obtain the layered modification through mechanochemistry. However, this was possible after optimizing the synthesis approach in terms of milling cycles and time. As a way of example, Figure S7 reports the pattern of \textit{Cs}_3\textit{Sb}_2\textit{I}_9 obtained at 400 rpm with 6 milling cycles which shows
a mixed sample composed of the two polymorphs. The present results show the first successful synthesis of layered Cs$_3$Sb$_2$I$_9$ by means of mechanochemistry approach.

![Image](image_url)

**Figure 7.** a) Photograph reporting the samples of Cs$_3$Sb$_2$Br$_{9-x}$I$_x$ solid solution; b) XRD patterns of the Cs$_3$Sb$_2$Br$_{9-x}$I$_x$ solid solution, c) XRD pattern of Cs$_3$Sb$_2$I$_9$ against the calculated structure of the layered polymorph (s.g. $P-3m1$)

Figure 7b reports the RT Cu-K XRD patterns of all the samples of the Cs$_3$Sb$_2$Br$_{9-x}$I$_x$ system, all in agreement with the $P-3m1$ s.g. A clear shift of all the peaks towards lower angles is evident by increasing the iodide content ($x$) according to an increase of the unit cell volume. All the samples result to be single phase and the patterns have been refined by Rietveld method and the lattice parameters and cell volume trend as a function of $x$ are shown in Figure 8 and listed in Table 3. Microprobe analysis resulted in a perfect agreement (within the e.s.d.) between nominal and effective halide contents.
Figure 8. Trend of (a) $a=b$ lattice parameter, (b) $c$ lattice parameter, and (c) cell volume for the samples of the Cs$_3$Sb$_2$Br$_9$I$_x$ solid solution as a function of $x$.

All the data follow a linear trend as a function of the iodide content, according to the Vegard’s law, confirming the formation of a continuous solid solution in this system in analogy with the analogous Bi-based system.$^{25,36}$
The observed expansion of the unit cell together with the progressive substitution of the Br atoms with a heavier one leads again to a clear redshift of the Raman modes, more pronounced with respect to what observed when Bi/Sb are replaced at the B sites, as above described. From Figure 9 this behavior is particularly evident for the mode at 210 cm\(^{-1}\) proper of the Cs\(_3\)Sb\(_2\)Br\(_9\) structure: its center shifted till 185 cm\(^{-1}\) for \(x = 6.5\) sample, then it completely disappears in the Cs\(_3\)Sb\(_2\)I\(_9\) compound.

Moving from one endmember to the other gradual changes are observed but it is more difficult to recognize a two-mode behavior probably caused by the higher disorder in the chemical distribution related to the specific site involved in the substitution. Moreover, as a consequence of the bandgap redshift, later discussed, the Raman intensity of \(x = 4.5, 6.5\) and 9 samples are strongly increased: indeed, these three samples start to absorb at 638 nm, namely the incident laser wavelength used to perform the characterization.

Finally, the Raman activity of Cs\(_3\)Sb\(_2\)I\(_9\) sample is consistent with the literature\(^{52,57}\). The spectrum is dominated by two intense features at 148.9 and 166.3 cm\(^{-1}\), once again assigned to the \(A_{1g}\) and \(E_g\) vibrational modes, involving both I and Sb atoms in the octahedral unit. Other less pronounced modes at 135.2 cm\(^{-1}\), 110.1 cm\(^{-1}\) and 85.3 cm\(^{-1}\) together with a broad feature at about 50 cm\(^{-1}\) are present. According to refs. 50 and 56, the lowest frequency modes, 85.3 cm\(^{-1}\) and the structure at 50 cm\(^{-1}\), are assigned to Sb-I bending and Sb-I-Sb interactions, respectively.

Table 3. Lattice parameters and band gap (BG) values for the Cs\(_3\)Sb\(_2\)Br\(_{9-x}\)I\(_x\) samples.

<table>
<thead>
<tr>
<th>(x)</th>
<th>(a=b) (Å)</th>
<th>(c) (Å)</th>
<th>Volume (Å(^3))</th>
<th>Direct BG (eV)</th>
<th>Indirect BG (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.9015(3)</td>
<td>9.7119(4)</td>
<td>525.12(4)</td>
<td>2.50</td>
<td>2.31</td>
</tr>
<tr>
<td>2.5</td>
<td>8.0760(3)</td>
<td>9.8875(4)</td>
<td>558.49(4)</td>
<td>2.21</td>
<td>1.87</td>
</tr>
<tr>
<td>4.5</td>
<td>8.1950(3)</td>
<td>10.0368(4)</td>
<td>583.74(4)</td>
<td>2.02</td>
<td>1.71</td>
</tr>
<tr>
<td>6.5</td>
<td>8.3037(3)</td>
<td>10.1642(4)</td>
<td>606.95(4)</td>
<td>1.98</td>
<td>1.70</td>
</tr>
<tr>
<td>9</td>
<td>8.4074(3)</td>
<td>10.3995(4)</td>
<td>636.61(4)</td>
<td>1.95</td>
<td>1.67</td>
</tr>
</tbody>
</table>
**Figure 9.** RT Raman spectra in the region between 25 and 250 cm$^{-1}$ for Cs$_3$Sb$_2$Br$_{9-x}$I$_x$ solid solutions as a function of $x$.

UV-vis absorption spectroscopy measurements on the Cs$_3$Sb$_2$Br$_{9-x}$I$_x$ system are reported in Figure 10a. There is a clear red shift by increasing the amount of iodide with a more pronounced effect up to $x=4.5$. The trend of direct and indirect band gap values as a function of iodide content is shown in Figure 10b.

**Figure 10.** (a) absorption spectra and (b) trend of the band gaps of the Cs$_3$Sb$_2$Br$_{9-x}$I$_x$ solid solution.
The values for the two end members are in agreement with those reported in the current literature. On the other hand, no previously data for Br/I mixed samples are available. Data in Figure 8b show a relevant initial reduction of the (direct) band gap from about 2.5 to 2.1 eV (at 50% of Br and I), followed by a smoother reduction of the band gap up to about 2.0 eV, showing again a bowing of the $E_g$. A similar alloying strategy was investigated on the Cs$_3$Bi$_2$Br$_9$. I$_x$ defective perovskites reporting as well a degree of band gap bowing which is, however, less pronounced with respect to the present Sb-based perovskites.
Conclusions

In the present work we explored two novel alloying strategies on the Cs$_3$Sb$_2$Br$_9$ defective perovskites, namely Sb/Bi and Br/I mixing. All the samples have been prepared for the first time (for these systems) by means of mechanochemistry route, indicating its suitability in providing single-phase materials and in preserving the stoichiometry (for both stoichiometric and alloyed samples). The variation of cell parameters for Cs$_3$(Sb$_{1-x}$Bi$_x$)$_2$Br$_9$ follows the Vegard’s law indicating the formation of a continuous solid solution. On the other hand, the trend of both direct and indirect band gaps shows a significant bowing and reduction for mixed Sb/Bi compositions, allowing to access band gap values lower than the two end-members, namely Cs$_3$Sb$_2$Br$_9$ and Cs$_3$Bi$_2$Br$_9$. This behavior has been modelled by DFT indicating that, for mixed systems, Sb and Bi aggregates control different regions of the electronic structure, showing a Sb-like valence band edge and a Bi-like conduction band edge, causing the drop in band gap at all mixing ratios.

For the Cs$_3$Sb$_2$Br$_9$-$_x$I$_x$ system we reported the first successful mechanochemical synthesis of the layered polymorph of Cs$_3$Sb$_2$I$_9$ perovskite, previously obtained only by high temperature solid state reaction. The Br/I alloying resulted in a linear expansion of the unit cell by increasing the I content confirming also in this case a full solubility of the two halides in the lattice. Absorption spectroscopy indicates a progressive red-shift by increasing $x$ with a pronounced bowing of the band gap from $x=4.5$ to $x=9$.

For both Cs$_3$(Sb$_{1-x}$Bi$_x$)$_2$Br$_9$ and Cs$_3$Sb$_2$Br$_9$-$_x$I$_x$ the Raman inspection allowed to confirm the single-phase structure of all the endmembers. Moreover, the reported results, confirmed by the XRD evidence, point out a redshift of the modes as a consequence of the cell expansion and the substitution of heavier ions that enlarged the reduced mass of the vibrational unit. The Raman features for the mixed samples are consistent with a two-mode behavior and the mixed phonon landscape which can in turn play an active role in the electronic response.
The present results provide a novel sustainable synthetic route to prepare Sb-based defective perovskites and, more importantly, two alloying strategies which allow to tune the band gap in most of the visible spectrum providing also the first evidence of band gap reduction by metal mixing (Sb/Bi) in a defective perovskite structure. Such effect has been only previously observed in double perovskites (Cs₂AgSbₓBi₁₋ₓBr₆) suggesting its possible universal character which is worth of being further explored in other related systems.
Supporting Information: Experimental Conditions, SEM images, additional XRD patterns, computational details.

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