Exploring the Transposition Effects on Electronic and Optics Properties of Cs$_2$AgSbCl$_6$ Using a Computational-Experimental Approach

Jun Zhou, Ximing Rong, Maxim S. Molokeev, Xiwen Zhang, Zhiguo Xia

ABSTRACT: The discovery of lead-free double perovskites provides a viable approach in the search for air-stable and environmental benign solar cells absorbers. Inspired by this, we have now prepared a double perovskite Cs$_2$AgSbCl$_6$, which is crystallized in cubic unit cell with space group Fm-3m and is found to have a varied band gap with different body colors. An anti-site defect model was established to investigate transposition influence on the optics and electronic properties of this double-perovskite Cs$_2$AgSbCl$_6$ structure. Moreover, Cs$_2$AgSbCl$_6$ perovskite has a high decomposition temperature and is stable upon prolonged exposure to air and moisture, which make it a potential absorber for photovoltaic and optoelectronic applications via further band gap engineering.

INTRODUCTION

In a remarkably short period of time, Pb-based halide perovskites have launched a new paradigm in the area of solution processable solar cells, surpassing polycrystalline and thin-film silicon photovoltaics, and achieving record power conversion efficiencies above 22%. The most extensively studied materials by far are the APbX$_3$ perovskites where A is an alkyl ammonium cation, such as CH$_3$NH$_3^+$, and X is halide ion (Cl$^-$, Br$^-$, or I$^-$). Despite their extremely outstanding solar cell performance, the toxicity of lead and the chemical instability of the lead halide perovskites impede their commercialization in the future. Given these limitations, searching for new air-stable and nontoxic lead-free halide perovskites via rational design is one of the key challenges to be addressed in the area of perovskite optoelectronics.

There are different structural design principles adopting in the search for potential Pb-replacements. One straightforward idea to solve the Pb toxicity issue involves replacing Pb$^{2+}$ by Sn$^{2+}$ and Ge$^{4+}$ from the same periodic group, but the chemical instability of Sn$^{2+}$ and Ge$^{4+}$ give rise to limitations for their further utilisation. Another promising approach to replace Pb is substitution of more stable cations, Br$^{3-}$ or Sb$^{5+}$, which is isoelectronic with Pb$^{2+}$, show great promise. However, the trivalent vs divalent oxidation state for the metal implies a need for vacancies on the metal site and therefore a lower dimensional structures and wider band gaps for the resulting A$_x$M$_y$VX$_y$ (A = K$^+$, Cs$^+$, Rb$^+$, [NH$_3$]$^+$ and [CH$_3$NH$_3$]$^+$; V = vacancy; M = Bi and Sb; X = Cl, Br and I$^-$).

However, the fact is that there are only a few bivalent or trivalent cations alternative to substitute Pb$^{2+}$ to form stable and non-toxic perovskites. Therefore, another viable route is the combination with a monovalent and a trivalent cation together, which leads to the formation of a double perovskite structure with a basic formula A$_x$B$^-$ B$^{+}$ $\times$ $\times$ (A = CH$_3$NH$_3^+$ or Cs$^+$; B$^-$ = Na$^+$, Cu$^+$ or Ag$^+$; B$^{+}$ = Bi$^{3+}$, Sb$^{5+}$ or In$^{3+}$; X = Cl, Br, or I$^-$. The double perovskites have been firstly investigated in the 1970s, initially in the context of ferroelectrics. Recently, in the light of the intense interest in halide perovskites, our group reported Cs$_2$AgInCl$_6$ with a band gap of 3.23 eV and it can be stable for several weeks in the air. Later, Tran et al. successfully control the direct vs. indirect nature of the band gap in halide perovskites by Cs$_2$AgSnIn$_2$Cl$_9$ solid solution. Here, we adopt hydrothermal method to grow pure Cs$_2$AgSbCl$_6$ crystals with varied band gaps, and we established an anti-site defect model by density functional theory (DFT) to investigate transposition influence on the electronic and optics properties of double-perovskite Cs$_2$AgSbCl$_6$ structure. Moreover, this Cs$_2$AgSbCl$_6$ crystal was also found to be stable for several weeks in the air and have a high decomposition temperature, which show great potential for photovoltaics and other optoelectronics application via further band gap engineering.

EXPERIMENTAL SECTION

Materials and Preparation. All the chemicals were commercially purchased and used without further purification. Crystals Cs$_2$AgSbCl$_6$ were synthesized by the hydrothermal method in a stainless steel Parr autoclave using 2.4 mmol CsCl, 1.2 mmol AgCl and 1.2 mmol SnCl$_4$ in 0.75 mL HCL acid solution. Powders of different colors from yellow to near black have been precipitated from solution upon heating at 453 K for 12 h. This solid was filtered out and then washed with ethanol and finally dried under reduced pressure overnight.

Characterization. The powder X-ray diffraction (XRD) measurements were conducted on a D8 Advance diffractometer (Bruker Corporation, Germany) operating at 40 kV and 40 mA with Cu Kα radiation (λ = 0.15406 Å), and the scanning rate was fixed at 4°/min. The powder diffraction pattern for Rietveld analysis was collected with the same diffractometer. The step size...
of 2θ was 0.016°, and the counting time was 1 s per step. Rietveld refinement was performed by using TOPAS 4.2 software. The morphology and crystalline size of the Cs$_2$AgSbCl$_6$ samples were determined by scanning electron microscope (SEM, JEOL JSM-6510). Diffuse reflectance spectra were measured on a UV-Vis-NIR spectrophotometer (SHIMADZU UV-3600) attached with an integrating sphere. BaSO$_4$ was used as a reference standard. Thermogravimetric analysis and differential scanning calorimetry (TG–DSC) were performed on a Setaram Labsys Evo at 10 °C min$^{-1}$ in an argon flow from room temperature to 1000 °C.

Computational methods. The band structure of Cs$_2$AgSbCl$_6$ is calculated by first-principles calculations using density functional theory (DFT), as implemented in the Vienna ab-initio simulation package (VASP) code. The projector augmented wave (PAW) potential method was used to describe the interactions between ions and electrons. The exchange–correlation interactions between electrons were treated within the generalized gradient approximation (GGA–PBE). The plane wave cut-off energy of 520 eV was used for all total energy calculations and structure optimization and the K-point meshes for different structures were generated according to the Monkhorst–Pack scheme for the Brillouin zones. To reduce the self-interaction error of DFT in band gap calculations, we used the Heyd - Scuseria - Ernzerhof (HSE) hybrid functional approach to evaluate the band gap and to compare with PBE functional approach.

RESULTS AND DISCUSSION

Crystalline Phase and Morphology. Figure 1a displays the observed (black), calculated (red), and the difference (grey) XRD profiles for Rietveld refinement of Cs$_2$AgSbCl$_6$. It is found that all peaks of the patterns were successfully indexed by cubic cell (Fm-3m) with parameters close to Cs$_2$AgAuCl$_6$ (elpasolite-type structure). As a comparison, site of Au in Cs$_2$AgAuCl$_6$ was occupied by Sb. Cs$_2$AgSbCl$_6$ belongs to the as-expected lead-free double perovskite, which crystallized in cubic unit cell with space group Fm-3m, and cell parameters, $a = 10.70093$ (6), $Z = 4$. The refinements of Cs$_2$AgSbCl$_6$ was stable, and the main parameters of processing and refinement with low $R$-factors are provided in Table 1, and the crystallographic information file (CIF) of Cs$_2$AgSbCl$_6$ is given in the supporting information (SI).

A visualization of the double perovskite structure is presented in Figure 1b, and the fractional atomic coordinates are also given in Table 2. Cs$_2$AgSbCl$_6$ exhibit a 3-dimensional framework of corner-sharing alternating octahedra of [AgCl$_6$] and [SbCl$_6$], with Cs$^+$ cations locating in the cavities formed between the octahedra, resulting in a doubled cell, i.e., elpasolite $K_2$NaAlF$_6$ structure, as also observed in Cs$_2$AgInCl$_6$. The Sb-Cl bond length (2.63(1) Å) is slightly shorter than that of Ag-Cl (2.72(1) Å), as it was expected.

![Figure 1](image1.png)

**Figure 1**: (a) Observed (black), calculated (red), and difference (gray) XRD profiles for the refinement of the Cs$_2$AgSbCl$_6$ sample using the Rietveld method. (b) Crystal structure of Cs$_2$AgSbCl$_6$ and coordination environments for Sb$^{5+}$, Ag$^+$, and Cl are given.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cs$_2$AgSbCl$_6$</th>
</tr>
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<tbody>
<tr>
<td>Sp.Gr.</td>
<td>Fm-3m</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>10.70093 (6)</td>
</tr>
<tr>
<td>$V$, Å$^3$</td>
<td>1225.36 (2)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
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<tr>
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<tr>
<td>$R_{wp}$, %</td>
<td>9.40</td>
</tr>
<tr>
<td>$R_B$, %</td>
<td>2.01</td>
</tr>
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</table>

**Table 1**: Main parameters of processing and refinement of the Cs$_2$AgSbCl$_6$ sample

![Figure 2](image2.png)

**Figure 2**: SEM images of Cs$_2$AgSbCl$_6$ crystals at (a) lower and (b) higher magnification.

It is also worth mentioning that the body colors of the as-prepared powders can be continuously changed from yellow to dark green and eventually to near black under the identical synthetic conditions (Figure 3a). Moreover, all of these samples are of pure phase, and this phenomenon cannot be controlled by the experimental conditions. Therefore, to determine the optical bandgaps for these different colored samples, the UV–vis diffuse reflection spectra of Cs$_2$AgSbCl$_6$ have been measured. As shown in Figure 3b, as the color of the samples deepens, the reflection curve becomes lower and lower. And the band gap of Cs$_2$AgInCl$_6$ can be estimated according to eq $^{26}$

$$F(R_e) = (1 - R)^2 / 2R = K/S$$  \hspace{1cm} (2)

where $h\nu$ is the photon energy; $A$ is a proportional constant; $E_r$ is the value of the band gap; $n = 2$ for a direct transition or 1/2 for an indirect transition; and $F(R_e)$ is the Kubelka-Munk function defined as $^{27}$

$$F(R_e) = (1 - R)^2 / 2R = K/S$$  \hspace{1cm} (2)
where $R$, $K$, and $S$ are the reflection, absorption, and scattering coefficient, respectively. From the linear extrapolation of $[F(R)\nu_0]^2=0$ in Figure 3c, we can estimate an indirect optical band gap in the range of 2.61 eV to 2.24 eV with the color changing from yellow to near black.

**Figure 3.** Powder XRD patterns (a), UV-vis diffuse reflectance spectra (b), and Tauce plots (c) of Cs$_2$AgSbCl$_6$ with very different visible light absorbance.

**Band Structure and Optical Absorption Calculations.** In order to further investigate this color-tunable phenomenon, we calculated the band structures using density functional theory (DFT). The details of the calculations are available in the Experimental section and the atomic structure used for the calculations is based on the X-ray diffraction data. Figure 4 shows the electronic band structure of double-perovskite Cs$_2$AgSbCl$_6$ by HSE (a) and PBE (b) calculation. Cs$_2$AgSbCl$_6$ showed an indirect band gap, with VBM at X (0.5, 0.5, 0) and CBM at L (0.5, 0.5, 0.5). The direct/indirect band gaps of primitive Cs$_2$AgSbCl$_6$ are 3.33/2.35 eV by HSE and 2.36/1.40 eV by PBE. As the electronic band structures by those two approaches only differ from the band gap, we choose PBE approach to quantitatively describe the defect influence on the electronic and optical properties of Cs$_2$AgSbCl$_6$ in the following investigations.

**Figure 4.** Electronic band structure of double-perovskite Cs$_2$AgSbCl$_6$ by HSE (a) and PBE (b) approach.

Since Ag and Sb have rather similar local environments in the present cubic double-perovskite Cs$_2$AgSbCl$_6$ phase, (e.g. Ag[Cl$_6$Sb$_8$Ag$_{12}$] and Sb[Cl$_6$Sb$_8$Ag$_{12}$] that differ only at the third shell, and similar atomic radii (0.16 nm for Ag and for 0.145 nm for Sb$^{2+}$)), it is worthwhile to study the anti-site defect between them. Furthermore, because we considered the anti-site defect with swapped Ag and Sb atoms, the ratio of every element will not be changed, making the defect structures possibly allomorphic. Figure 5a shows a diagrammatic sketch of two anti-site defect models of Cs$_2$AgSbCl$_6$ structures based on a primitive (with rhombic structure) enlarged $2 \times 2 \times 2$ super cell (Cs$_{16}$Ag$_6$Sb$_8$Cl$_{48}$). In these two anti-site models, an Ag atom makes atomic transposition with its nearest neighbor (NN) Sb and second-nearest neighbor (2NN) Sb atom. Before selecting the size of the super cell, we tested the size effect of the defect energy, as shown in Figure 5b. For NN and 2NN structures, $E_{\text{defect}}$ has been converged according with the results of $2 \times 2 \times 2$ and $3 \times 3 \times 3$ super cells, meaning that the $2 \times 2 \times 2$ super cell is large enough to avoid boundary effect caused by DFT calculation.

**Figure 5.** (a) Diagrammatic sketch of two anti-site defect models of Cs$_2$AgSbCl$_6$ structures. NN: transposition of Ag and its nearest neighbor Sb atom; 2NN: transposition of Ag and its second-nearest neighbor Sb atom. (b) Energy per defect for NN and 2NN structures for $2 \times 2 \times 2$ and $3 \times 3 \times 3$ Cs$_2$AgSbCl$_6$ super cells.
Figure 6 shows the electronic band structures of NN (Fig. 6a) and 2NN (Figure 6b) Cs$_6$AgSbCl$_8$ anti-site structures from the PBE calculations. The direct band gaps of the anti-site structures are decreased from 2.36 eV (pristine) to 1.36 eV (NN) and 1.13 eV (2NN). The decreasing of the direct gap from NN to 2NN anti-sites reflects the effect of the local electric field between the oppositely charged Ag and Sb anti-site defects. Details of band gaps are presented in Table 4. As NN and 2NN are allotropes of double-perovskite Cs$_6$AgSbCl$_8$ structures, the obvious gap differences indicate that this defect model could stand a good chance in the experiments.

Figure 6c shows the imaginary part of the dielectric functions of 3 Cs$_6$AgSbCl$_8$ structures. The absorption edges as coincided with the direct band gaps (see Table 4), showed $E_{\text{balanced}} > E_{\text{NN}} > E_{\text{2NN}}$, which are in consist with the band gap variation of these structures. As we discussed before, since a significant amount of anti-sites with NN, 2NN, ... nearest neighbor configurations would form at the experimental temperature, Cs$_6$AgSbCl$_8$ would have strong optical absorption for photons with energy much lower than its pristine optical band gap. It would be hard to define strictly the actual optical gap of defective Cs$_6$AgSbCl$_8$. However, the optical absorbance of defective Cs$_6$AgSbCl$_8$ to visible light (below its optical band gap of ~3.33 eV according to HSE calculations) can be continuously varied due to the formation of anti-site defects. Indeed, in experiment, we observed almost continuously constant optical absorbance for most visible light in Cs$_6$AgSbCl$_8$ below its pristine optical band gap (see Fig. 3b) indicated by a clear optical absorption shoulder that doesn’t change much for different samples (the variation of optical gap from 2.61 to 2.24 eV could not explain the significant variation of sample colors). The main different between the samples with different colors is the magnitude of reflectance for visible light (see the right side of Fig. 3b, i.e. the darker sample absorbs (reflects) more (less) visible light. A possible reason is that the darker sample contains more Ag-Sb anti-site defects. The above optical absorption feature is rather different than the widely studied tune-ability of sample color by controlling sizes of nanocrystals (e.g. in Ref. 27), where the optical absorption shoulder changes significantly for different samples with different nano-crystal sizes. In our experiments, we also observed slight variation of optical absorption shoulders, which may reflect the change of nano-crystal sizes. Furthermore, although there are contributions from phonon assistant absorption in Fig. 3b, phonon effect could not explain the sharp variation of sample colors since phonon assistant absorption could not go below the fundamental gap of pristine Cs$_6$AgSbCl$_8$ (2.35 eV according to HSE calculations) much. The tune-ability of visible light absorbance in Cs$_6$AgSbCl$_8$ induces variety of colors of the materials, and could have further implications for optical properties.
2NN) are thermodynamically stable with only 7–12 meV/atom larger than balanced structure, and the band gap could be relatively varied with rarely small lattice expansion. Overall, the discovery of Cs$_2$AgSbCl$_6$ furthermore stress on the importance of the double perovskite approach in the search for lead-free photovoltaic materials that exhibit good stability.

**AUTHOR INFORMATION**

**Corresponding Author**
* E-mail: xiuwenzhang@szu.edu.cn (Y. Zhang)
* E-mail: xiaozg@ustb.edu.cn (Z. Xia)

**Author Contributions**
* These authors contributed equally.

**Notes**
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