Exploring the transposition effects on the electronic and optical properties of Cs$_2$AgSbCl$_6$ via a combined computational-experimental approach†

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The electronic and optical properties of perovskites are related to the local structures of the compounds and define their functional applications. Herein we have prepared a double perovskite Cs$_2$AgSbCl$_6$, which crystallized in the cubic structure with the space group Fm$\overline{3}$m and the material is found to have a varied band gap associated with different body colors. The anti-site defect model was established to investigate transposition influence on the optical and electronic properties of the double-perovskite Cs$_2$AgSbCl$_6$, and the proposed model clearly explained the as-observed variable body color. Cs$_2$AgSbCl$_6$ perovskite has a high decomposition temperature and is stable upon prolonged exposure to air and moisture, which emphasize its potential in the field of photovoltaic absorbers and optoelectronic applications.

1 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%.$^{1-3}$ The most extensively studied materials by far are the APbX$_3$ perovskites where A is an alkyl ammonium cation CH$_3$NH$_3$$^+$ or Cs$^+$ ion, and X is a halide ion (Cl$, $Br$, $I$).$^{4,5}$ 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.$^6$ 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 field of perovskite optoelectronics.$^{7}$

There are different structural design principles adopted in the search for potential Pb-replacements. One straightforward idea to solve the Pb toxicity issue involves replacing Pb$^{2+}$ by Sn$^{2+}$ from the same periodic group, but the chemical instability of Sn$^{2+}$ and poor performance give rise to limitations for their further use.$^{8,9}$ Another promising approach to replace Pb is substitution by more stable cations, Bi$^{3+}$ or Sb$^{3+}$, which is isoelectronic with Pb$^{2+}$. However, the change of divalent to trivalent metal oxidation state implies a need for vacancies on the metal site and therefore lower dimensional structures and wider band gaps for the resulting A$_{2}$B$_{2}$VX$_{6}$ (A $=$ K$^+$, Cs$^+$, Rb$^+$, [NH$_4$]$^+$ and [CH$_3$NH$_3$]$^+$; V = vacancy; M = Bi and Sb; X = Cl, Br and I).$^{10,11}$ Nevertheless, the fact is that there are only a few bivalent or trivalent cations alternative to Pb$^{2+}$ that form stable and non-toxic perovskites.$^{12}$ Therefore, another viable route is combination with a monovalent and a trivalent cation together, which leads to the formation of a double perovskite structure with the basic formula A$_{2}$B$^\text{II}$B$^\text{III}$X$_{6}$ (A $=$ CH$_3$NH$_3$$^+$ or Cs$^+$; B$^\text{II}$ = Na$^+$, Cu$^+$ or Ag$^+$; B$^\text{III}$ = Bi$^{3+}$, Sb$^{3+}$ or In$^{3+}$; X = Cl$, $Br$, or I$^-$).$^{13-15}$ The double perovskites were first investigated in the 1970s, initially in the context of ferroelectrics.$^{16}$ 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 air.$^{17}$ Later, Tran et al. successfully controlled the direct $\text{vs.}$ indirect nature of the band gap in halide perovskites in Cs$_2$AgSb$_{1-x}$In$_x$Cl$_6$ solid solution.$^{18}$ Herein, we adopted a hydrothermal method to grow pure Cs$_2$AgSbCl$_6$ crystals with a varied...
band gap, and we established an anti-site defect model by density functional theory (DFT) to investigate transposition influence on the electronic and optical properties of the double-perovskite Cs$_2$AgSbCl$_6$. This site-equivalent transposition, which easily occurred during the experimental process, did not change the atomic ratio and had a big influence on the band gap. Moreover, the Cs$_2$AgSbCl$_6$ crystal was found to be stable in air for several weeks and has a high decomposition temperature. This material shows great potential for optoelectronics application via further band gap engineering.

2 Experimental section

2.1 Materials and preparation

All the chemicals were commercially purchased and used without further purification. Crystals of Cs$_2$AgSbCl$_6$ were synthesized by the hydrothermal method in a stainless steel Parr autoclave using 2.4 mmol CsCl (99.99%, Aladdin), 1.2 mmol AgCl (99.5%, Aladdin) and 1.2 mmol SbCl$_3$ (99.9%, Aladdin) in a certain amount (0.5 mL to 1.5 mL) of HCl acid solution (99.5%, Beijing Chemical Works). The powders with colors from yellow to near black by alternating the volume of the solution (99.5%, Beijing Chemical Works). The powders with

2.2 Characterization

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$^{-1}$. 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 microscopy (SEM, JEOL JSM-6510). The diffuse reflectance spectra were measured on a UV-Vis-NIR spectrophotometer (SHIMADZU UV-3600) supplied 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.

2.3 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) 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 the PBE functional approach.

3 Results and discussion

3.1 Crystalline phase and morphology

Fig. 1a displays the observed (black), calculated (red), and the difference (grey) XRD profiles for the Rietveld refinement of Cs$_2$AgSbCl$_6$. It is found that all peaks of the patterns were successfully indexed to a cubic cell (Pm-3m) with parameters close to Cs$_2$AgAuCl$_6$ (elpasolite-type structure). In comparison, the site of Au in Cs$_2$AgAuCl$_6$ is occupied by Sb. Cs$_2$AgSbCl$_6$ belongs to the as-expected lead-free double perovskite family, crystallizes in the cubic unit cell with the space group Pm-3m, and cell parameters, a = 10.70093 Å, Z = 4. The refinements of Cs$_2$AgSbCl$_6$ were stable, and the main parameters of processing and refinement with low R-factors are provided in Table 1. The crystallographic information file (CIF) of Cs$_2$AgSbCl$_6$ is given in the ESL. Further details of the crystal structure may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; E-mail: crystdata@fiz-karlsruhe.de; http://www.fiz-karlsruhe.de/request_for_deposited_data.html on quoting the deposition numbers: CSD-433743).

A visualization of the double perovskite structure is presented in Fig. 1b, and the fractional atomic coordinates are also given in Table 2. Cs$_2$AgSbCl$_6$ exhibits a 3-dimensional framework of corner-sharing alternating octahedra of [AgCl$_6$] and [SbCl$_6$], with Cs$^+$ cations located in the cavities formed between the octahedra, resulting in a double 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 expected.

Fig. 2a shows the typical SEM images of the as-prepared Cs$_2$AgSbCl$_6$ microcrystals, which are comprised of numerous uniform rhombic dodecahedron particles with a size of 15–60 μm. A closer observation of the magnified images for one microcrystal (Fig. 2b) demonstrates that the rhomic
dodecahedron shows the typical fcc-crystal features, a tetradecahedral crystallization habit forming a truncated octahedral. Besides, the exhibited facets of Cs₂AgSbCl₆ were determined to be (100) and (111). Additionally, the well faceted microcrystal shapes generally indicate the high structural quality of the powder product, as obtained for several other compounds.

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 with increasing volumes of HCl from 0.5 mL to 1.5 mL (Fig. 3a). Moreover, all of these samples are pure phase, and this phenomenon can be controlled by the added amount of HCl in the reaction solution. To determine the optical bandgaps for these different colored samples, the UV-vis diffuse reflection spectra of Cs₂AgSbCl₆ have been measured. As shown in Fig. 3b, as the color of the samples deepens, the reflection curve becomes lower and lower. The band gap of Cs₂AgSbCl₆ can be estimated according to eqn (1)²⁰

$$[F(R_w)hv]^n = A(hv - E_g)$$

where $hv$ is the photon energy; $A$ is a proportional constant; $E_g$ is the value of the band gap; $n = 2$ for a direct transition or 1/2 for an indirect transition; and $F(R_w)$ is the Kubelka-Munk function defined as³¹

$$F(R_w) = (1 - R)^2/2R = K/S$$

where $R$, $K$, and $S$ are the reflection, absorption, and scattering coefficient, respectively. From the linear extrapolation of $[F(R_w)hv]^{1/2} = 0$ in Fig. 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.

### 3.2 Band structure and optical absorption calculations

In order to further investigate this color-tuning 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. Fig. 4 shows the electronic band structure of the double-perovskite Cs₂AgSbCl₆ by HSE (a) and PBE (b) calculations. Cs₂AgSbCl₆ 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

Table 1 Main parameters of processing and refinement of the Cs₂AgSbCl₆ sample

| Compound     | Cs₂AgSbCl₆ |
|--------------|------------|
| Sp.Gr.       | Fm-3m      |
| $a$, Å       | 10.70093 (6) |
| $V$, Å³      | 1225.36 (2)  |
| $Z$          | 4          |
| 2θ-interval, ° | 5–120       |
| $R_{wlp}$, % | 11.57       |
| $R_p$, %     | 8.39        |
| $R_{exp}$, % | 9.40        |
| $\rho_{calc}$, | 1.23       |
| $R_B$, %     | 2.01        |

Table 2 Fractional atomic coordinates and isotropic displacement parameters (Å²) of Cs₂AgSbCl₆

|      | x     | y     | z     | $B_{iso}$ |
|------|-------|-------|-------|-----------|
| Cs   | 1/4   | 1/4   | 1/4   | 2.71 (9)  |
| Ag   | 1/2   | 1/2   | 1/2   | 1.6 (1)   |
| Sb   | 0     | 0     | 0     | 1.1 (1)   |
| Cl   | 0.2456 (11) | 0   | 0     | 3.1 (1)   |

Fig. 2 (a) Typical SEM images of Cs₂AgSbCl₆ crystals, (b) one representative microcrystal showing different facets.
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 obtained by these two approaches differ only in the band gaps, we choose the PBE approach to quantify the defect influence on the electronic and optical properties of Cs$_2$AgSbCl$_6$ in the following investigations.

Since Ag and Sb have rather similar local environments in the present cubic double-perovskite Cs$_2$AgSbCl$_6$ phase (e.g. Ag $[\text{Cl}_6\text{Cs}_8\text{Sb}_6\text{Ag}_{12}]$ and Sb$[\text{Cl}_6\text{Cs}_8\text{Ag}_6\text{Sb}_{12}]$ that differ only in the third shell, and similar atomic radii (0.16 nm for Ag and 0.145 nm for Sb)), 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 each element will not be changed, making the defect structures possibly allomorphic. Fig. 5a shows a diagrammatic sketch of two anti-site defect models of Cs$_2$AgSbCl$_6$ structures based on a primitive (with a rhombic structure) enlarged $2 \times 2 \times 2$ super cell ($\text{Cs}_{16}\text{Ag}_8\text{Sb}_8\text{Cl}_{48}$). In these two anti-site models, an Ag atom makes atomic transposition with its nearest neighbor (NN) Sb atom 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 Fig. 5b. For NN and 2NN structures, $E_{\text{defect}}$ has been converged in accordance 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 the boundary effect caused by DFT calculations. And the structural parameters of primitive Cs$_2$AgSbCl$_6$ and 3 Cs$_{16}$Ag$_8$Sb$_8$Cl$_{48}$ (balanced, NN and 2NN) structures after full relaxation are shown in Table 3. Compared with the balanced structures, the lattices of NN and 2NN defect structures expanded and the total energy was increased by 0.625 eV (NN) and 0.975 eV (2NN) due to the influence of the internal defect on the lattice. For the NN anti-site model, the structure is no longer cubic, this is mainly because the transposition occurred within the diagonal of the face rather than the body diagonal, causing the lattice to expand uncoordinated with a distortion. For the 2NN anti-site model, the lattice also slightly expands (by 0.39%). Due to the relatively low formation energy of anti-site defects (e.g. 0.625 eV for the NN anti-site), a significant amount of Ag–Sb anti-site defects would form. The Ag and Sb anti-site defects would be connected to their NN, 2NN, 3NN,... neighboring anti-sites in the crystal.

Fig. 6 shows the electronic band structures of NN (Fig. 6a) and 2NN (Fig. 6b) Cs$_{16}$Ag$_8$Sb$_8$Cl$_{48}$ anti-site structures from the PBE calculations. (c) Imaginary part of the dielectric functions of 3 Cs$_{16}$Ag$_8$Sb$_8$Cl$_{48}$ structures from the PBE calculations.

Table 3 Structural parameters of primitive Cs$_2$AgSbCl$_6$ and 3 Cs$_{16}$Ag$_8$Sb$_8$Cl$_{48}$ (balanced, NN and 2NN) structures

| Structure | $E_{\text{tot}}$ (eV) | $\Delta E$ (eV) | $\Delta E$/atom (meV) | $V$ ($\text{Å}^3$) | $L_a$ ($\text{Å}$) | $L_b$ ($\text{Å}$) | $L_c$ ($\text{Å}$) | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) |
|-----------|-----------------|----------------|---------------------|-------------|----------------|----------------|----------------|-------------|-------------|-------------|
| Primitive | $-32.703$        | $-$           | $-$                 | $319$       | $7.672$        | $7.672$        | $7.672$        | $60$         | $60$         | $60$         |
| Balanced  | $-261.625$      | $0$           | $0$                 | $2554$      | $15.343$       | $15.343$       | $15.343$       | $60$         | $60$         | $60$         |
| NN        | $-261.000$      | $0.625$       | $7.81$              | $2586$      | $15.397$       | $15.424$       | $15.397$       | $59.94$      | $60.12$      | $59.94$      |
| 2NN       | $-260.650$      | $0.975$       | $12.19$             | $2584$      | $15.403$       | $15.403$       | $15.403$       | $60$         | $60$         | $60$         |
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$_2$AgSbCl$_6$ structures, the obvious gap differences indicate that this defect model could stand a good chance in the experiments.

Fig. 6c shows the imaginary optical absorption coefficient of the dielectric functions of 3 Cs$_{16}$Ag$_8$Sb$_8$Cl$_{48}$ structures. The absorption edges coincided with the direct band gaps (see Table 4) and showed the order $E_{\text{NN}} > E_{\text{2NN}}$, which is consistent with the band gap variation in 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$_2$AgSbCl$_6$ would have strong optical absorption for photons with energy much lower than its experimental optical gap $E_g$. The variety of optical absorbance of Cs$_2$AgSbCl$_6$ containing defects could not go below the fundamental gap of pristine Cs$_2$AgSbCl$_6$ [2.35 eV according to HSE calculations]. The variety of visible light absorbance in Cs$_2$AgSbCl$_6$ is related to the observed colors of the materials, which also have some implications for optical properties.

### 3.3 Chemical, light and thermal stability

Regarding the environmental stability of Cs$_2$AgSbCl$_6$, the selected Cs$_2$AgSbCl$_6$ sample with $E_g = 2.61$ eV was exposed to the ambient atmosphere under both light and moisture conditions, with the powder XRD and UV-vis diffuse reflectance spectra monitored as a function of time (Fig. 7). It is found that there is nearly no apparent difference in the thermal and chemical stability depending on the crystal size. Hence, as can be seen in Fig. 7a, the powder XRD patterns for one month storage (in the ambient atmosphere) show no evidence of material decomposition, indicating that the material is rather stable. As for the reflectance spectrum, no obvious change was detected in the curve shape except for the slight intensity decline (Fig. 7b).

Halide perovskites are known for low decomposition and formation energies. Since thermal stability is also an important parameter for halide perovskites in the prospective applications, we carried out thermogravimetric and differential scanning calorimetry (TG-DSC) analysis of a Cs$_2$AgSbCl$_6$ powder sample (Fig. 8). From the recorded TG-DSC result during the heat-treatment of Cs$_2$AgSbCl$_6$ in an argon flow, it is apparent that there are two major stages of rapid weight loss in the TGA.

![Fig. 7 PXRD patterns (a) and UV-vis diffuse reflectance spectra (b) of Cs$_2$AgSbCl$_6$ after 0 days, 7 days, 14 days, 21 days, 28 days and 35 days of exposure to light and moisture conditions.](image)

![Fig. 8 TGA and DSC data for a powder sample of Cs$_2$AgSbCl$_6$.](image)

| Table 4 Band gap of Cs$_2$AgSbCl$_6$ for different anti-site defect models and calculation methods |
|-----------------------------------------------|
| Structure | Calculation method | $E_{g}^{\text{direct}}$/eV | $E_{g}^{\text{indirect}}$/eV | $E_{g}^{\text{overall}}$/eV |
|-----------|-------------------|-----------------|-----------------|-----------------|
| Primitive | HSE               | 3.33            | 2.35            | 2.35            |
| Primitive | PBE               | 2.36            | 1.40            | 1.40            |
| NN        | PBE               | 1.36            | ---             | 1.36            |
| 2NN       | PBE               | 1.13            | 0.90            | 0.90            |
curve at 356 and 756 °C, accompanying their corresponding exothermic peaks, which indicates that Cs₂AgSbCl₆ may decompose by two steps. The first weight loss of about 28.55 wt%, observed at 250–500 °C, is ascribed to the evaporation of SbCl₃. Notably, SbCl₃ constitutes 32.21% of the total weight of Cs₂AgSbCl₆ and therefore, the decomposition reaction equation might be described as follows: Cs₂AgSbCl₆ → SbCl₃ + Cs₂AgCl₃. Finally, the third serious weight loss of 42.64 wt%, observed at 500–1000 °C and centered at around 756 °C, is in good agreement with the theoretical value of CsCl (47.55%) evaporation, and the decomposition process could proceed according to the scheme below: Cs₂AgCl₃ → AgCl + 2CsCl. The above results showed that Cs₂AgSbCl₆ is relatively stable to mass loss up to 250 °C. After that, some obvious decomposition reaction occurs enabling the materials to lose the functionality completely.

4 Conclusion

In summary, we have designed and prepared phase pure crystals of Cs₂AgSbCl₆ via hydrothermal routes, which is relatively stable and non-toxic and has a low band gap. To demonstrate the transposition influence on the electronic and optical properties of Cs₂AgSbCl₆, focusing a combined experimental and theoretical study, we established an anti-site defect model by density functional theory (DFT). By exchanging site-equal Ag and Sb ions, the two allotropes (NN and 2NN) are thermodynamically stable with only 7–12 meV per atom larger than the balanced structure, and the band gap could be varied with relatively small lattice expansion. Overall, the discovery of Cs₂AgSbCl₆ furthermore stresses the importance of the double perovskite approach in the search for lead-free photovoltaic materials that exhibit good stability.

Conflicts of interest

There are no conflicts to declare.

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