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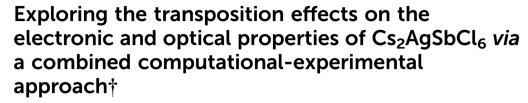


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The electronic and optical properties of perovskites are related to the local structures of the compounds and define their functional applications. Herein we have prepared a double perovskite Cs₂AgSbCl₆, which crystallized in the cubic structure with the space group *Fm*-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 Cs₂AgSbCl₆, and the proposed model clearly explained the as-observed variable body color. Cs₂AgSbCl₆ 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.

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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 APbX₃ perovskites where A is an alkyl ammonium cation CH₃NH₃⁺ 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 $A_3M_2VX_9$ ($A = K^+$, Cs^+ , Rb^+ , $[NH_4]^+$ and $[CH_3NH_3]^+$; V = vacancy; M = Bi and Sb; X = Cl, Br and II, II,

Nevertheless, the fact is that there are only a few bivalent or trivalent cations alternative to Pb²⁺ that form stable and non-toxic perovskites. 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 $A_2B'B''X_6$ ($A = CH_3NH_3^+$ or Cs^+ ; $B' = Na^+$, Cu^+ or Ag^+ ; $B'' = Bi^{3+}$, Sb^{3+} or In^{3+} ; $X = Cl^-$, Br^- , or I^-). The double perovskites were first investigated in the 1970s, initially in the context of ferroelectrics. Recently, in the light of the intense interest in halide perovskites, our group reported $Cs_2AgInCl_6$ with a band gap of 3.23 eV and it can be stable for several weeks in air. Later, Tran *et al.* successfully controlled the direct νs . indirect nature of the band gap in halide perovskites in $Cs_2AgSb_{1-x}In_xCl_6$ solid solution. Herein, we adopted a hydrothermal method to grow pure $Cs_2AgSbCl_6$ crystals with a varied

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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 Cs₂AgSbCl₆. This site-equal 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 Cs₂-AgSbCl₆ 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.

Experimental section

Materials and preparation

All the chemicals were commercially purchased and used without further purification. Crystals of Cs2AgSbCl6 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 SbCl₃ (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 added HCl were precipitated from solution during the hydrothermal reaction at 453 K over 12 h. This solid product was filtered out, washed with ethanol and finally dried under reduced pressure overnight.

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 K α 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.19 The morphology and crystalline size of the Cs₂AgSbCl₆ 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. BaSO₄ 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 2.3

The band structure of Cs2AgSbCl6 is calculated by firstprinciples calculations using density functional theory (DFT), as implemented in the Vienna ab initio simulation package (VASP) code. 20,21 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).22,23 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 scheme24 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 approach²⁵ to evaluate the band gap and to compare with the PBE functional approach.

3 Results and discussion

Crystalline phase and morphology

Fig. 1a displays the observed (black), calculated (red), and the difference (grey) XRD profiles for the Rietveld refinement of Cs₂AgSbCl₆. It is found that all peaks of the patterns were successfully indexed to a cubic cell (Fm-3m) with parameters close to Cs₂AgAuCl₆ (elpasolite-type structure).²⁶ In comparison, the site of Au ion in Cs₂AgAuCl₆ is occupied by Sb. Cs₂AgSbCl₆ belongs to the as-expected lead-free double perovskite family, crystallizes in the cubic unit cell with the space group Fm-3m, and cell parameters, a = 10.70093 (6), Z = 4. The refinements of Cs₂AgSbCl₆ 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 Cs2AgSbCl6 is given in the ESI.† 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. Cs₂AgSbCl₆ exhibits a 3-dimensional framework of corner-sharing alternating octahedra of [AgCl₆] and [SbCl₆], with Cs⁺ cations located in the cavities formed between the octahedra, resulting in a double cell, i.e., elpasolite K₂NaAlF₆ structure, as also observed in Cs₂AgInCl₆.¹⁷ 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 Cs₂AgSbCl₆ 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 rhombic

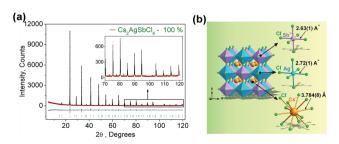


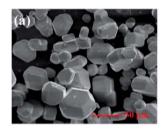
Fig. 1 (a) Observed (black), calculated (red), and difference (gray) XRD profiles for the refinement of the Cs₂AgSbCl₆ sample using the Rietveld method. (b) Crystal structure of Cs₂AgSbCl₆ and coordination environments for Sb³⁺, Ag⁺, and Cl⁻ are given.

Table 1 Main parameters of processing and refinement of the Cs_2 -AqSbCl₆ sample

Compound	$\mathrm{Cs_2AgSbCl_6}$
Sp.Gr.	Fm-3m
a, Å	10.70093 (6)
V , $\mathring{\mathbf{A}}^3$	1225.36 (2)
Z	4
2θ -interval, $^{\circ}$	5-120
R_{wp} , %	11.57
R _p , %	8.39
$R_{\rm exp}$, %	9.40
$R_{\rm exp}$, % χ^2	1.23
R_{B} , %	2.01

Table 2 Fractional atomic coordinates and isotropic displacement parameters (Å 2) of $\rm Cs_2AgSbCl_6$

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



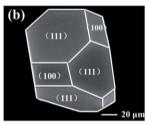


Fig. 2 (a) Typical SEM images of $Cs_2AgSbCl_6$ crystals, (b) one representative microcrystal showing different facets.

dodecahedron shows the typical fcc-crystal features, a tetrade-cahedral crystallization habit forming a truncated octahedral. Besides, the exhibited facets of $Cs_2AgSbCl_6$ 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. ^{27–29}

It is also worth mentioning that the body colors of the asprepared 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 Cs₂-AgSbCl₆ 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 $(1)^{30}$

$$[F(R_{\infty})hv]^n = A(hv - E_g) \tag{1}$$

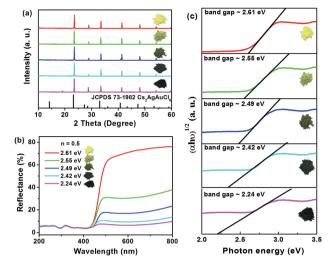


Fig. 3 Powder XRD patterns (a), UV-vis diffuse reflectance spectra (b), and Tauc plots (c) of different as-prepared $Cs_2AgSbCl_6$ obtained by using different amounts of HCl (0.5, 0.75, 1.0, 1.25 and 1.5 mL) with variable visible light absorbance.

where $h\nu$ is the photon energy; A is a proportional constant; $E_{\rm g}$ is the value of the band gap; n=2 for a direct transition or 1/2 for an indirect transition; and $F(R_\infty)$ is the Kubelka–Munk function defined as³¹

$$F(R_{\infty}) = (1 - R)^2 / 2R = K/S \tag{2}$$

where R, K, and S are the reflection, absorption, and scattering coefficient, respectively. From the linear extrapolation of $[F(R_\infty) hv]^{1/2} = 0$ 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 Cs₂-AgSbCl₆ 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

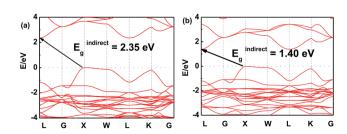


Fig. 4 Electronic band structure of the double-perovskite $Cs_2AgSbCl_6$ by HSE (a) and PBE (b) approaches.

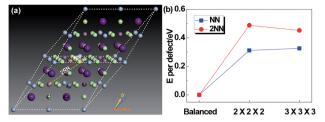


Fig. 5 (a) Diagrammatic sketch of the two anti-site defect models of Cs₂AgSbCl₆ structures. NN: transposition of Ag and its nearest neighbor Sb atom; 2NN: transposition of Ag and its second-nearest neighbor Sb atom. (b) Energy per defect for NN and 2NN structures for $2 \times 2 \times 2$ and $3 \times 3 \times 3$ Cs₂AqSbCl₆ super cells.

primitive Cs₂AgSbCl₆ 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 Cs₂AgSbCl₆ in the following investigations.

Since Ag and Sb have rather similar local environments in the present cubic double-perovskite Cs2AgSbCl6 phase (e.g. Ag [Cl₆Cs₈Sb₆Ag₁₂] and Sb[Cl₆Cs₈Ag₆Sb₁₂] that differ only in the third shell, and similar atomic radii (0.16 nm for Ag and 0.145 nm for Sb³²)), it is worthwhile to study the anti-site defect between them. Furthermore, because we considered the antisite 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 Cs2AgSbCl6 structures based on a primitive (with a rhombic structure) enlarged $2 \times 2 \times 2$ super cell (Cs₁₆Ag₈Sb₈Cl₄₈). 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, $E_{\rm defect}$ 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 Cs₂AgSbCl₆ and 3 Cs₁₆Ag₈Sb₈Cl₄₈ (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

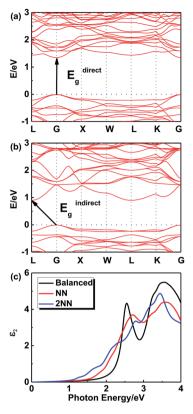


Fig. 6 Electronic band structure of NN (a) and 2NN (b) Cs₁₆Ag₈Sb₈Cl₄₈ anti-site structures from the PBE calculations. (c) Imaginary part of the dielectric functions of 3 Cs₁₆Ag₈Sb₈Cl₄₈ structures from the PBE calculations

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) Cs₁₆Ag₈Sb₈Cl₄₈ anti-site structures from the PBE calculations, respectively. Since a super cell is required in the process of calculating defects, the band folding will occur and result in the gap fold of the band structure to the gamma point, so direct band gap is chosen to be discussed. The direct band gaps of the anti-site structures decrease from 2.36 eV (pristine) to 1.36 eV (NN) and 1.13 eV (2NN). The decrease of the direct gap from NN to 2NN anti-sites reflects the effect of the

Table 3 Structural parameters of primitive Cs₂AgSbCl₆ and 3 Cs₁₆Ag₈Sb₈Cl₄₈ (balanced, NN and 2NN) structures

Structure	$E_{\rm tot}$ (eV)	ΔE (eV)	ΔE/atom (meV)	$V(\mathring{A}^3)$	$L_{\mathrm{a}}\left(\mathring{\mathrm{A}}\right)$	$L_{\mathrm{b}}\left(\mathring{\mathrm{A}}\right)$	$L_{\mathrm{c}}(\mathring{\mathrm{A}})$	α (°)	β (°)	γ (°)
Primitive Balanced	-32.703 -261.625	_ 0	_	319 2554	7.672 15.343	7.672 15.343	7.672 15.343	60 60	60 60	60 60
NN 2NN	-261.023 -261.000 -260.650	0.625 0.975	7.81 12.19	2586 2584	15.397 15.403	15.424 15.403	15.397 15.403	59.94 60	60.12 60	59.94 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 $\mathrm{Cs_2AgSbCl_6}$ 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 Cs₁₆Ag₈Sb₈Cl₄₈ structures. The absorption edges coincided with the direct band gaps (see Table 4) and showed the order $E_{\rm balanced} > E_{\rm NN} > E_{\rm 2NN}$, 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, Cs₂AgSbCl₆ 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 Cs2AgSbCl6 containing defects. However, the optical absorbance of Cs2AgSbCl6 containing defects towards visible light (below its optical band gap of \sim 3.33 eV according to HSE calculations) can be continuously varied due to the formation of anti-site defects. Indeed, in the experiments, we observed almost continuously constant optical absorbance for most of the visible light in Cs₂AgSbCl₆ 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 difference 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 more visible light, in other words it reflects less light. A possible reason is that the darker sample contains more Ag-Sb anti-site defects. Since 100% Ag-Sb anti-sites in Cs₂AgSbCl₆ lead to the same structure as the pristine crystal and zero defect formation energy, in local regions of Cs₂AgSbCl₆, clusters of Ag-Sb anti-sites could form, leading to high anti-site density. The formation of anti-site clusters is hard to control precisely in the current synthesis of bulk compounds. The above optical absorption feature is rather different from the widely studied tunability of sample color by controlling the sizes of nano-crystals (e.g. in ref. 33), where the optical absorption shoulder changes significantly for different samples with different nano-crystal sizes. In our experiments, we also observed a slight variation of optical absorption shoulders, which may reflect the change of nano-crystal sizes. Furthermore, although there are contributions from phonon assisted absorption in Fig. 3b, the phonon effect could not explain the sharp sample color variation since phonon assisted

 $\label{eq:table 4} \mbox{ Band gap of Cs_2AgSbCl}_6 \mbox{ for different anti-site defect models} \\ \mbox{and calculation methods}$

Structure	Calculation method	$E_{ m g}^{ m direct}/{ m eV}$	$E_{ m g}^{ m indirect}/{ m eV}$	$E_{ m g}^{ m overall}/{ m eV}$
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

absorption could not go below the fundamental gap of pristine Cs₂AgSbCl₆ (2.35 eV according to HSE calculations). The variety of visible light absorbance in Cs₂AgSbCl₆ is related to the asobserved colors of the materials, which also have some implications for optical properties.

3.3 Chemical, light and thermal stability

Regarding the environmental stability of $Cs_2AgSbCl_6$, the selected $Cs_2AgSbCl_6$ 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 Cs₂AgSbCl₆ powder sample (Fig. 8). From the recorded TG-DSC result during the heat-treatment of Cs₂AgSbCl₆ in an argon flow, it is apparent that there are two major stages of rapid weight loss in the TGA

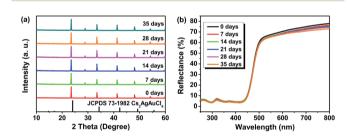


Fig. 7 PXRD patterns (a) and UV-vis diffuse reflectance spectra (b) of $Cs_2AgSbCl_6$ after 0 days, 7 days, 14 days, 21 days, 28 days and 35 days of exposure to light and moisture conditions.

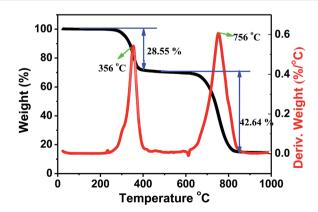


Fig. 8 TGA and DSC data for a powder sample of Cs₂AgSbCl₆.

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.34 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.

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 Cs₂-AgSbCl₆ 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.

Acknowledgements

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