Theoretical exploration of mechanical, electronic structure and optical properties of aluminium based double halide perovskite

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1 Introduction

Perovskites are a series of ABX$_3$-type materials named after a Russian mineralogist Lev Perovski, such as CaTiO$_3$ and BaTiO$_3$, and originally used for ferroelectric and piezoelectric materials. For the last decade, perovskites have been studied for photovoltaic and optoelectronic purposes due to their appropriate energy band structures and good light absorption. T. Miyasaka et al. made the earliest application of organic–inorganic perovskite materials in dye-sensitized solar cells in 2009. However, at the first, they did not attract much attention because of the low efficiency and poor stability until N. G. Park et al. reported a perovskite solar cell with power conversion efficiency over 9% and 500 hour stability in air conditions. From then, perovskite solar cells became a very popular objective and many perovskite lead-free materials have been explored by experiments and theoretical studies. Several preliminary studies were carried out with attractive results and redrew attention to chalcogenide perovskite AZrS$_3$, which exhibits great absorbing properties of Cs$_2$AgBiX$_6$ (X = Cl, Br) materials have been studied since 2016 and used as photocatalysts in CO$_2$ reduction and H$_2$ evolution. Cs$_2$AgInCl$_6$ has been synthesized and applied in the field of organic degradation and fast ultraviolet detectors. Cs$_2$AgSbCl$_6$ shows a superior blue photoluminescence quantum yield of 31.33%, and excellent air stability. Therefore, it is assumed that cesium–silver based perovskites are potential in optoelectronics field. Cai et al. have given out a primary high-throughput computational study of Cs$_2$MM’Cl$_6$. Cs$_2$InBiCl$_6$ and Cs$_2$InSbCl$_6$ have been considered as candidate for traditional MAPbI$_3$ because of their proper direct band gap. However, they have not been synthesized yet as a result of the extreme instability of In$^+$ ions. On the other hand, Cs$_2$AgSbCl$_6$ and Cs$_2$AgInCl$_6$ have been considered by both experiment and theoretical calculation. Recently, the properties of similar Cs$_2$CuBiX$_6$ have been calculated by density functional theory. The results show that these materials with indirect band gap are not suitable for photoelectronic devices. From the advance studies, it is predicted that Cs$_2$AgMCl$_6$ (M = Al, Ga, In, Tl) have direct band structures. Thus, In- and Ga-based materials were reported to exhibit suitable direct bandgaps within the optimal range of 0.9–1.6 eV, preferable to previous Ag/Bi based double perovskites, showing a promising utilization prospect. With similar electronic structure, aluminium and thallium element are of great potential to substitute for indium and gallium as well. Tl-based perovskite materials have already experimentally and theoretically characterized and show a relatively outstanding light absorption and carrier mobility. However, the application of thallium is
under strict control due to the high toxicity of this heavy metal element. Up to now, although few researchers focused on perovskite containing aluminium, the aluminium compound AlCl₃ has been successfully introduced into perovskite material to improve the photoluminescence and photoresponse.³⁵ Consequently, considering the abundant amount and low toxicity, only Al-based double halide perovskite were studied by density functional theory (DFT) calculation in this paper. Furthermore, there is a conflict between small reserves of cesium and its huge demand in high tech field, such as atomic clocks, drilling fluid and ion propulsion engine, which indicates that reserves of cesium may not meet the large-scale application of photoelectronic devices. Hence, we also discuss the properties of substitutable alkali metal Rb₂AgAlBr₆ and K₂AgAlBr₆ to explore the feasibility of these two materials.

2 Computational methods

All geometry optimizations, electronic structures, mechanical properties and optical properties are carried out by DFT methods within the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA-PBE) as implemented in the Cambridge Sequential Total Energy Package (CASTEP) based on Materials Studio software.²⁶,²⁷ The OTFG ultrasoft pseudo-potential is adopted to describe the electron–ion interactions. The Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm was adopted to optimize the crystal structures. For geometric optimization, a 8 × 8 × 8 Monkhorst–Pack grid²⁸ is used and a plane wave kinetic energy cut-off of 600 eV is chosen, and all structures are relaxed until the forces on the atoms are less than 0.03 eV Å⁻¹ while the total energy change becomes less than 1.0 × 10⁻⁵ eV, crystal internal stress is less than 0.05 GPa and maximum displacement of atoms is less than 0.001 Å. Due to the discontinuity of exchange–correlation energy, the GGA-PBE function often underestimates the energy band value of compounds,²⁹,³⁰ a more accurate hybrid HSE06 functional with norm-conserving pseudo-potential is used to correct the electronic structures and optical properties.³¹,³² In addition, the energy cutoff and k-point mesh were set to 700 eV and 4 × 4 × 4, respectively.

3 Results and discussion

3.1 Crystal structure and thermodynamics stability

For conventional ABX₃ perovskites, the structure is usually cubic-centered. Therefore, in this paper, the theoretical models of double halide perovskite are built as Fm3m space group, and there are two cations at B sites (B' and B") with oxidation states of +1 and +3, which may have different orderings. As shown in Fig. 1, in a unit cell of double perovskite structure, the A site is occupied with Cs⁺, Rb⁺ or K⁺, the +1 B' sites and +3 B" sites are initialized with Ag⁺ and Al³⁺, respectively, and X is halogen anion (Cl⁻, Br⁻ or I⁻). The calculated lattice constants are shown to be 10.11 Å, 10.65 Å, 11.47 Å, 10.57 Å and 10.52 Å for Cs₂AgAlCl₆, Cs₂AgAlBr₆, Cs₂AgAlBr₆, Rb₂AgAlBr₆, and K₂AgAlBr₆, respectively. It is obvious that the lattice constants increase with the increased atomic number of halogen anions and alkali cations.

In perovskite, the Goldschmidt tolerance factor is widely used as a reliable test for the formation of perovskite structure, which is defined as \( t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \), where \( r_A \), \( r_B \) and \( r_X \) represent the radii of the A site cation, B site cation and X site anion, respectively. Generally, perovskite structures tend to form in the range of 0.8 ≤ t ≤ 1.0 while perovskite with t in the range of 0.9–1.0 tends to have a perfect structure.³³–³⁵ In this work, the Shannon ionic radii³⁶ are used, and similar to previous work on A site alloying, the average of radii of the two B site cations as \( r_B \), that is, \( r_B = \frac{1}{2}(r_{B'} + r_{B''}) \). The calculated Goldschmidt tolerance factors \( t \) are listed in Table 1. All the results of \( t \) values are within the best range, confirming the perfect perovskite structure.

In addition, to study the thermodynamics stability of these perovskites, the formation energy \( E_f \) and the binding energy \( E_b \) are calculated using the following formula:³⁷

\[
E_f = E_{M_2AgAlX_6} - n_M \times \mu_M - n_{Ag} \times \mu_{Ag} - n_{Al} \times \mu_{Al} - n_X \times \mu_X
\]

\[
E_b = E_{M_2AgAlX_6} - n_M \times E_M - n_{Ag} \times E_{Ag} - n_{Al} \times E_{Al} - n_X \times E_X
\]

where \( E_{M_2AgAlX_6} \) is the total energy of perovskite crystals, \( E_M, E_{Ag}, E_{Al} \) and \( E_X \) are the energy of single alkali metal, Ag, Al and halogen atoms, respectively. The \( \mu \) represents the chemical potential of individual atom and the \( n \) represents the number of atoms. The results are listed in Table 1. Except from the formation energy of Cs₂AgAlI₆, the other values are all negative, which indicates that Cs₂AgAlI₆ may not be thermodynamic stable and is difficult to be synthesized through experiment. However, the \( E_f \) change from positive to negative for halogen atom varied from Br to I. Generally, there may be some stable structure of iodine doped Cs₂AgAlBr₆, namely Cs₂AgAlBr₆₋ₓ. Moreover, the lower the formation energy means that the structure is more stable,⁴⁰
which reveals that Cs$_2$AgAlCl$_6$ is the most stable among the studied materials.

3.2. Elastic properties

Elastic constants are important and interesting parameters linked to the physical properties of solid materials. Due to the symmetry of cubic structures, the independent stiffness constants are reduced to 3, which are $C_{11}$, $C_{12}$ and $C_{44}$ respectively. Other elastic constants are also given in Table 2 in detail, including bulk modulus ($B$), shear modulus ($G$), Young modulus and Poisson ratio. Our results are only for reference due to the lack of previous study. These values seem to be low due to the lack of previous study. These values seem to be low

In addition, the anisotropy of materials can be studied by the criteria of the elastic anisotropy coefficient $A$ proposed by Zener:

$$A = \frac{2C_{44}}{C_{11} - C_{12}}$$

If the $A$ value is 1, the perovskite materials have isotropic physical properties, otherwise it is anisotropic. Neither the elastic anisotropy coefficient of all materials equals to 1, meaning that they are all anisotropic and have distinct properties in different directions while Cs$_2$AgAlBr$_6$ have the most isotropic properties.

3.3. Band structure and density of states

The band structure of perovskites is very important for optoelectronic devices. In order to understand the electronic properties of perovskites, the band structure were corrected using HSE06 functional and depicted in Fig. 2. It can be seen that both valence band maximum (VBM) and conduction band minimum (CBM) located at gamma point in Brillouin zone. All the perovskite materials have direct band structure which is beneficial for the carrier transition between VBM and CBM. This is similar to the previous results based on In-containing double perovskites.

The band gap values vary from 0.773 eV to 3.430 eV, just in the ideal energy gap range of semiconductor. The halogen anions have a great influence on the band gap value while alkali metal does not. In general, the band gap value can be modulated to a certain extent by alloying or doped with other elements. Besides, the hydrostatic pressure is another effective tool that can bring about band gap variation.

### Table 2: The calculated elastic properties of double perovskite M$_2$AgAlX$_6$ (M = Cs, Rb or K; X = Cl, Br or I)

| Composition | $C_{11}$ (GPa) | $C_{12}$ (GPa) | $C_{44}$ (GPa) | $B$   | $G$   | $B/G$ | $A$   | Young modulus (GPa) | Poisson ratio |
|-------------|----------------|----------------|----------------|-------|-------|-------|-------|---------------------|--------------|
| Cs$_2$AgAlCl$_6$ | 46.78          | 25.52          | 14.60          | 32.61 | 12.86 | 2.54  | 1.37  | 34.09               | 0.33         |
| Cs$_2$AgAlBr$_6$ | 45.38          | 20.46          | 11.86          | 28.77 | 12.10 | 2.38  | 0.95  | 31.83               | 0.32         |
| Cs$_2$AgAlI$_6$ | 39.85          | 16.09          | 10.25          | 24.01 | 10.87 | 2.21  | 0.86  | 28.34               | 0.30         |
| Rb$_2$AgAlBr$_6$ | 49.51          | 19.54          | 10.61          | 29.53 | 12.19 | 2.42  | 0.71  | 32.14               | 0.32         |
| K$_2$AgAlBr$_6$ | 50.17          | 19.20          | 9.17           | 29.52 | 11.33 | 2.61  | 0.59  | 30.13               | 0.33         |

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Meanwhile, total densities of states and partial densities of states are also plotted in Fig. 3 and help to understand the variation of electronic structure and optoelectronic properties. The contribution to the hybridization and inter-band transition comes from valence electrons, and their contribution near the Fermi surface is shown in Fig. 3. The Cs cation makes little contribution to the VBM and plays nearly no role in the dispersion of CBM. The valence band maximum is dominated mainly by X-p orbitals and partially by Ag-d orbitals, whereas conduction bands are in an anti-bonding manner predominated by the Al-s/p orbitals with the Br-p orbital.\textsuperscript{61} According to the previous study,\textsuperscript{27} comparing with Cu and Au, Ag-containing compounds have larger band gaps due to the lowest-energy d states and the VBM derives from hybridization between Cu/Ag/Au-d and Cl-p orbitals.\textsuperscript{60} For the M = Ag series, for M’ = Ga, In, Tl, the CBM is derived from anti-bonding M’-s and Cl-p states. Cs$_2$AgAlCl$_6$ has the largest band gap because Al-s state is shallow, and the hybridization of Al-Cl is strong, leading to a high-lying Al-Cl anti-bonding level. In this case, the CBM is no longer Al-Cl states but Ag-Cl states.

The effective mass of holes ($m_{h}^*$) and electrons ($m_{e}^*$) is a critical electronic property which has great effect on the separation efficiency and the mobility of photogenerated carriers.\textsuperscript{63} It can be obtained by the following formula:\textsuperscript{63}

$$m^* = \hbar^2 \left[ \frac{\partial^2 E(k)}{\partial^2 k} \right]^{-1}$$

where $E(k)$ and $k$ represent the eigenvalues of energy band and the wave vector along different directions, respectively. And $\hbar$ is reduced Planck constant. The effective masses near VBM and CBM in different direction are most attractive and calculated in this paper, while $m_0$ represents the inertial mass of an electron. As shown in Table 3, the effective masses of electrons and holes of these perovskite materials are very small, and only the $m_{h}^*$ of Cs$_2$AgAlCl$_6$ along the $G \rightarrow X$ direction is slightly large than $m_0$, showing an advantage in carrier transport. Along the $G \rightarrow L$ and $G \rightarrow X$ directions, the values of effective mass of carriers gradually decrease in the order of Cs$_2$AgAlCl$_6$, Cs$_2$AgAlBr$_6$, and Cs$_2$AgAlI$_6$, so does the value in the order of Cs$_2$AgAlBr$_6$, Rb$_2$AgAlBr$_6$, and K$_2$AgAlBr$_6$. It is evident both the smaller alkali metal atom and larger halogen atom help to decrease the effective mass and improve the electronic properties.\textsuperscript{62,64,65}

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Fig. 2  The energy band structure of (a) Cs$_2$AgAlCl$_6$, (b) Cs$_2$AgAlBr$_6$, (c) Cs$_2$AgAlI$_6$, (d) Rb$_2$AgAlBr$_6$, and (e) K$_2$AgAlBr$_6$ calculated by hybrid HSE06 functional.
3.4. Optical properties

The optical properties play an essential role for optoelectronic materials and should be analyzed in some detail. Generally, the complex dielectric function is described by

\[ \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \]

where \( \varepsilon_1(\omega) \) represents the real part of dielectric function and \( \varepsilon_2(\omega) \) represents the imaginary part of the dielectric function. The real part \( \varepsilon_1(\omega) \) usually depicts the polarization degree of medium under an external electric field and can be deduced from the Kramers–Kronig relationship. As for the real part \( \varepsilon_1(0) \), it usually depicts the electron transitions from occupied states to unoccupied states while light passing through a medium, and it can be obtained by the momentum matrix of electronic transitions. Other important optical parameters such as refractive index \( n(\omega) \) and extinction coefficient \( k(\omega) \) can be deduced through the complex dielectric function. The calculated \( \varepsilon_1(0) \), \( \varepsilon_2(0) \) spectra, refractive index \( n(\omega) \) and extinction coefficient \( k(\omega) \) of \( \text{M}_2\text{AgAlX}_6 \) are shown in Fig. 4.

Fig. 4(a) and (b) show the curves of \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \), respectively. The static dielectric constants \( \varepsilon_1(0) \) are respectively 2.61, 3.03, 3.95, 2.93 and 2.87 in the order of Cs\(_2\)AgAlCl\(_6\), Cs\(_2\)AgAlBr\(_6\), Cs\(_2\)AgAlI\(_6\), Rb\(_2\)AgAlBr\(_6\), and K\(_2\)AgAlBr\(_6\). Static values of \( \varepsilon_1(0) \) and band gap \( (E_g) \) are according to the Penn’s model \( \varepsilon_1(0) = 1 + \left(\frac{\hbar^2}{m_0^*} E_p^2\right)^\frac{1}{2} \)

Table 3  The effective mass of holes \( (m_0^*) \) and electrons \( (m_e^*) \)

| Materials | Directions | \( m_0^* \/ m_0 \) | \( m_e^* \/ m_0 \) |
|-----------|------------|-------------------|-------------------|
| G → L     | G → L      | G → X             | G → X             |
| Cs\(_2\)AgAlCl\(_6\) | 0.321 | 1.091 | 0.126 | 0.167 |
| Cs\(_2\)AgAlBr\(_6\) | 0.211 | 0.320 | 0.091 | 0.091 |
| Cs\(_2\)AgAlI\(_6\) | 0.200 | 0.153 | 0.055 | 0.054 |
| Rb\(_2\)AgAlBr\(_6\) | 0.201 | 0.284 | 0.094 | 0.094 |
| K\(_2\)AgAlBr\(_6\) | 0.194 | 0.265 | 0.094 | 0.094 |

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where \( \varepsilon_1(\omega) \) represents the real part of dielectric function and \( \varepsilon_2(\omega) \) represents the imaginary part of the dielectric function. The real part \( \varepsilon_1(\omega) \) usually depicts the polarization degree of medium under an external electric field and can be deduced from the Kramers–Kronig relationship. As for the real part \( \varepsilon_1(0) \), it usually depicts the electron transitions from occupied states to unoccupied states while light passing through a medium, and it can be obtained by the momentum matrix of electronic transitions. Other important optical parameters such as refractive index \( n(\omega) \), extinction coefficient \( k(\omega) \), \( L(\omega) \) and \( \sigma(\omega) \) can be deduced through the complex dielectric function. The calculated \( \varepsilon_1(0) \), \( \varepsilon_2(0) \) spectra, refractive index \( n(\omega) \) and extinction coefficient \( k(\omega) \) of \( \text{M}_2\text{AgAlX}_6 \) are shown in Fig. 4.

Fig. 4(a) and (b) show the curves of \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \), respectively. The static dielectric constants \( \varepsilon_1(0) \) are respectively 2.61, 3.03, 3.95, 2.93 and 2.87 in the order of Cs\(_2\)AgAlCl\(_6\), Cs\(_2\)AgAlBr\(_6\), Cs\(_2\)AgAlI\(_6\), Rb\(_2\)AgAlBr\(_6\), and K\(_2\)AgAlBr\(_6\). Static values of \( \varepsilon_1(0) \) and band gap \( (E_g) \) are according to the Penn’s model \( \varepsilon_1(0) = 1 + \left(\frac{\hbar^2}{m_0^*} E_p^2\right)^\frac{1}{2} \)

Then as the photon energy increases, the \( \varepsilon_1(\omega) \) of Cs\(_2\)AgAlCl\(_6\), Cs\(_2\)AgAlBr\(_6\), Cs\(_2\)AgAlI\(_6\), Rb\(_2\)AgAlBr\(_6\), and K\(_2\)AgAlBr\(_6\) reach their maximum values at 6.54 eV, 5.63 eV, 4.32 eV, 5.81 eV and 5.86 eV, respectively. The maximum values of these compounds gradually increase as the anion changes from Cl\(^-\) to
Br\(^-\) and then to I\(^-\) and slightly increase cation changes from K\(^+\) to Rb\(^+\) and then to Cs\(^+\). It is noteworthy that there are negative values of \(\varepsilon(\omega)\) between 15.33 and 20.76 eV for Cs\(_2\)AgAlCl\(_6\), 15.60–19.73 eV for Cs\(_2\)AgAlBr\(_6\), 9.73–12.13 eV and 15.73–18.95 eV for Cs\(_2\)AgAlI\(_6\), 12.65–13.70 eV and 21.54–22.15 eV for Rb\(_2\)AgAlBr\(_6\) and 12.69–14.84 eV for K\(_2\)AgAlBr\(_6\), which means that strong reflection and the photons in these energy range can not transport in the materials.

The \(\varepsilon(\omega)\) spectra of the M\(_2\)AgAlX\(_6\) materials are related to their behavior of light absorption. The thresholds of light absorption shift to lower photon energy with decrease in bandgap values of the studied compounds. The main peaks appear in the energy range lower than 10.5 eV with their peak positions respectively locating at 10.51, 9.15, 7.54, 9.28 and 9.50 eV in the order of Cs\(_2\)AgAlCl\(_6\), Cs\(_2\)AgAlBr\(_6\), Cs\(_2\)AgAlI\(_6\), Rb\(_2\)AgAlBr\(_6\) and K\(_2\)AgAlBr\(_6\). The main peaks locating in the deep-ultraviolet light range are composed of electronic transitions from the top valence bands to the conduction bands far away from the Fermi surface. It may indicate the potential of ultraviolet-light detector and photocatalytic.

The complex refractive indexes of solids can be described by \(n(\omega) = n(\omega) + ik(\omega)\), where \(n(\omega)\) is the refractive index and \(k(\omega)\) is the extinction coefficient. The refractive index \(n(\omega)\) illustrates the dispersion of light when falling on material surface. As depicted in Fig. 4(c) and (d), we can see that \(n(\omega)\) and \(k(\omega)\), respectively, have the similar variation trends as \(\varepsilon(\omega)\) and \(\varepsilon(\omega)\). From Fig. 4(a), the calculated static refractive indexes \(n(0)\) are respectively 1.61, 1.74, 1.98, 1.71 and 1.69 for Cs\(_2\)AgAlCl\(_6\), Cs\(_2\)AgAlBr\(_6\), Cs\(_2\)AgAlI\(_6\), Rb\(_2\)AgAlBr\(_6\) and K\(_2\)AgAlBr\(_6\). It is obvious that \(n(\omega)\) values of M\(_2\)AgAlX\(_6\) perovskites gradually increase and reach the maximum at the range of 8–10 eV. The range \(n(\omega)\) less than \(K(\omega)\) means that no photons in this energy region can be transported in the materials. The result is consistent with the dielectric function \(\varepsilon(\omega)\). The calculated reflectivities \(R(\omega)\), loss function \(\ell(\omega)\), conductivity \(\sigma(\omega)\) and absorption coefficient \(a(\omega)\) of M\(_2\)AgAlX\(_6\) are shown in Fig. 5.

Fig. 5(a) displays the reflectivities of M\(_2\)AgAlX\(_6\) double perovskites. The calculated static reflection coefficients \(R(\omega)\) for M\(_2\)AgAlX\(_6\) double perovskites are, respectively, 0.055, 0.073, 0.109, 0.069 and 0.066 for Cs\(_2\)AgAlCl\(_6\), Cs\(_2\)AgAlBr\(_6\), Cs\(_2\)AgAlI\(_6\), Rb\(_2\)AgAlBr\(_6\) and K\(_2\)AgAlBr\(_6\). However, except from the \(R(\omega)\) of Cs\(_2\)AgAlCl\(_6\), their values are very small in the observed energy region, and even the maximum values of M\(_2\)AgAlX\(_6\) in the range of energy smaller than 10 eV regions are around 0.25, that is, most photons in this energy region can be absorbed by the materials or pass through the materials instead of being reflected by the materials.

The loss functions \(\ell(\omega)\) of M\(_2\)AgAlX\(_6\) double perovskites were shown in Fig. 5(b), revealing the energy loss of a fast electron passing through a material. It indicates that loss functions for M\(_2\)AgAlX\(_6\) double perovskites are very small with their maximum value of ~0.3 in the visible and ultraviolet light range (~10 eV).

The calculated real part of optical conductivity of the M\(_2\)AgAlX\(_6\) compounds are presented in Fig. 5(c) to investigate their optical response, which is caused by the conduction of electrons in the compounds. It can be found that Cs\(_2\)AgAlI\(_6\) shows the largest \(\sigma(\omega)\) in the lower photon energy range of 0–9.0 eV among the studied compounds, while the \(\sigma(\omega)\) of Cs\(_2\)AgAlCl\(_6\) is the largest in the photon energy range of 10.20–16.90 eV.
Absorption coefficient $a(\omega)$ is an important parameter of optoelectronic materials. As shown in Fig. 5(d), all the $a(\omega)$ of studied materials are small in the visible wavelength and sharply increase from 5 eV of the photon energy, meaning that the materials have strong responses to photon in ultraviolet wavelength and can work in this condition. The absorption edges shift with the same regularity with the band gaps. From 3.0–14.0 eV, the variations of $M_2AgAlBr_6$ are in broad agreement, indicating similar optical responses and the possibility of cheaper K atom substitute for Cs atom.

4 Conclusions

In this paper, aluminium based double halide perovskite $M_2AgAlX_6$ were optimized and calculated by DFT. The thermodynamic and mechanical stabilities of $M_2AgAlX_6$ perovskite were checked through Born–Huang stability criterion and confirmed by calculating the tolerance factor, the formation energy and the binding energy except for $Cs_2AgAlI_6$, indicating the possibility of experimental synthesis and commercial application. Elastic constants analysis shows that the studied materials are all ductile and suitable for flexible optoelectronic devices. All the materials have direct band structures. The energy band gap varies from 0.773 eV to 3.430 eV, and the substitution of alkali metal atoms does not change the band gap. The band gap can be modulated by halogen atom doping.

The effective masses of all materials are very small in both $G \rightarrow L$ and $G \rightarrow X$ direction, which is conducive to carrier mobility. The optical properties show the materials have strong optical response in ultraviolet wavelength and may be applied for ultraviolet detector and photocatalytic. Cheaper K atoms substitute derivatives have similar properties as Cs-based materials, which show the potential of large-scale utilization.

Conflicts of interest

The authors have no conflicts to disclose.

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