First-principles study of (CsMA)NaSbX₆ (MA = methylammonium; X = Cl, Br, I) organic–inorganic hybrid double perovskites for optoelectronic applications

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Abstract

Significant interests have been drawn to organic–inorganic hybrid double perovskites towards the commercialization of Pb-free non-toxic perovskites because of their unique optoelectronic properties compared to their inorganic counterparts. In this study, the structural, electronic and optical properties, as well as stability, of (CsMA)NaSbX₆ (MA = methylammonium; X = Cl, Br, I) were investigated using first-principles density functional theory (DFT). Results of the DFT method reveal that the investigated compounds have tunable bandgaps, high absorption coefficients and high refractive indices. Our findings also show that the iodide-based compound, (CsMA)NaSbI₆, shows superior optoelectronic properties compared to the bromide- and chloride-based compounds, (CsMA)NaSbBr₆ and (CsMA)NaSbCl₆. Specifically, results of the study predict the (CsMA)NaSbI₆ organic–inorganic hybrid double perovskite to be a promising candidate for optoelectronic applications due to its high absorption coefficient (on the order of 10⁶ cm⁻¹), dielectric constant (approx. 4.43), and refractive index (2.83) as well as the high formation energy depicting its stability. These results can be utilized for synthesis of sustainable and non-toxic optoelectronic devices.

Keywords Organic · Inorganic · Double · Perovskite · Optoelectronics

1 Introduction

As the quest for new affordable and more efficient materials for use in optoelectronic applications, such as photovoltaics, is increasing, materials scientists are expanding the field by modifying existing material systems or developing new ones entirely. These new materials, perovskites, have shown good traits for stable performance and have high prospects of becoming good and stable candidates for photovoltaics [12]. Perovskites refer to a group of compounds with the general formula ABX₃, where A is usually an inorganic or organic cation (Cs⁺ or CH₃NH₃⁺), B is a metal cation (Pb²⁺) and X is a halogen anion (I⁻, Br⁻ or Cl⁻), and they are among emerging crystals with unique optoelectronic characteristics such as tunable electronic bandgap, high optical absorption with broad spectrum, good photoconductivity, low carrier effective masses with high mobility, and extended charge diffusion lengths with high lifetimes [11, 12].

Recently, great interest has been drawn to double perovskites with the basic formula AₓB′B″X₆, where A is a cation typically, Cs⁺ or methylammonium (MA⁺), B′ is a trivalent metal cation such as Bi³⁺ or Sb³⁺, B″ is a monovalent metal usually Cu⁺, Ag⁺, or Au⁺ and X is usually a halide such as Cl⁻, Br⁻ or I⁻ [5, 15, 17, 19]. This shift in focus is largely because of the instability of lead-halide perovskites, and these materials offer a suitable replacement for lead [17]. Moreover, better optoelectronic properties have been observed for MA-based organic–inorganic hybrid perovskites compared to Cs-containing inorganic perovskites as well as a similarity in optoelectronic properties of Cs₂BiAgI₆ and Cs₂SbAgI₆ with MAPbI₃ [12, 17]. Nonetheless, of all reviewed hybrid double perovskites [1, 9, 10], the use of a noble metal is paramount. In these studies, Cu or Ag have been largely employed as B″ site element; however, due to the depletion of copper ore [14] and the high cost of silver, the present work seeks to explore Na as a B″ site element while investigating different combinations to find a suitable replacement for Pb in double perovskite and, as such,
establish the usability in different applications. This choice of Na is attributed to the fact that, of the noble metals, Ag (1.02 Å) has an ionic radius that is closest to that of Na (1.15 Å) [16, 17]. To curb the cost associated with the precursors, CuCl, AgCl, and AuCl, required for the synthesis of inorganic double perovskites [17], from which hybrid organic–inorganic double perovskites are formed, this study investigates the feasibility of (CsMA)NaSbX₆ (X = Cl, Br, I) organic–inorganic hybrid double perovskites for use in optoelectronic applications using the first-principles density functional theory (DFT) method.

2 Computational method

The DFT calculations were performed using the Quantum ESPRESSO (QE) package implemented in Materials Square [7]. The ultrasoft pseudopotential including core correction was used for all calculations. The exchange–correlation energy was evaluated through the local density approximation (LDA) of Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation [13]. In order to overcome the underestimation of bandgaps obtained within LDA-PBE, the hybrid Heyd–Scuseria–Ernzerhof (HSE) [4] functional was also used for the band structure calculations. Moreover, to optimize the crystal structure and estimate the ground state energy, the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization technique was used.

In this study, the plane-wave cutoff energy and charge density were set at 30 Ry and 180 Ry, respectively, throughout the calculation. To sample the Brillouin zone, the Monkhorst–Pack scheme k point of 4 × 4 × 4 was used for all calculations associated with LDA-PBE to obtain the best convergence and total energy value, and the k point of 2 × 2 × 2 was used for calculations associated with HSE. All investigated cells were fully relaxed until the cell stresses were at least 10⁻⁶ Ry/bohr³ and the residual forces on each atomic site were at least 10⁻⁴ Ry/bohr.

3 Results and discussion

3.1 Structural properties

The optimized lattice parameters for the studied hybrid double perovskites are listed in Table 1. These Sb-based hybrid inorganic and organic double perovskites show increasing trend in order from X = Cl, Br and I.

From Table 1, it can be inferred that the bandgap energy increases with a decrease in lattice constants in accordance with the observation by [3, 11] that the replacement of a halogen atom (X) by a lighter and smaller halogen atom reduces the lattice parameter. Generally, the halogens increase in atomic size down the group in the Periodic Table [6, 18], and as such, increasing the halide concentration results in a decrease in the bandgap energy. The bandgap of the investigated perovskites can be tuned by changing the halogen content. This characteristic spurs usability in areas such as light emitting diodes (LEDs) [11, 12].

3.2 Electronic properties

The electronic band structures for the hybrid double perovskite compounds are shown in Figs. 1, 2, 3. These hybrid double perovskites were predicted to be of an indirect-bandgap type like their inorganic double perovskites, Cs₂NaBX₆ (B = Bi, Sb; X = Cl, Br, I) [16]. The conduction band minima (CBMs) were shown to appear at the X point of the high-symmetry path of the Brillouin zone with the exception of (CsMA)NaSbI₆, with its CBM at the R point of the Brillouin zone. On the other hand, the valence band maxima (VBMs) of these materials were found to be at the M point. The calculated bandgap values are presented in Table 1, from which it can be inferred that the iodide hybrid double perovskite ((CsMA)NaSbI₆) (2.09 eV) exhibits the smallest bandgap value. These values are comparable to that of Cs₂AgBiBr₆ (2.19 eV by measurement) [8]. Moreover, all the perovskites in the present method have bandgap values of 2.09 eV for (CsMA)NaSbI₆, 3.05 eV for (CsMA)NaSbCl₆, and 2.55 eV for (CsMA)NaSbBr₆. These values are comparable to that of (MA)₂BiAgCl₆ (2.7 eV) [17] within the same level of theory and MAPbCl₃ (3.0 eV) [8], apart from (CsMA)NaSbCl₆ (3.1 eV) in the present study, which shows slight deviations which could be attributed to its small value of lattice parameter as opined by [3]. Nonetheless, owing to the fact that among the three hybrid organic–inorganic double perovskites investigated, the hybrid double perovskite (CsMA)NaSbI₆ shows a similar dielectric constant as MAPbI₃, further investigations were done to delineate its electronic properties using HSE to curb the bandgap underestimation by the LDA-PBE scheme as shown in Fig. 4. The band structure obtained shows that the double perovskite (CsMA)NaSbI₆ is an indirect-bandgap material with minimum bandgap value of 2.09 eV for LDA-PBE and 2.29 eV for HSE methods in Fig. 4a.

| Compounds          | α (Å)  | (eV) (LDA-PBE) |
|--------------------|--------|----------------|
| (CsMA)NaSbCl₆      | 7.75   | 3.05           |
| (CsMA)NaSbBr₆      | 8.17   | 2.55           |
| (CsMA)NaSbI₆       | 8.77   | 2.09           |
Looking at the curves for band structures obtained by LDA-PBE and HSE, it can be inferred that both curves have a similar pattern, with only a slight shift in the CBM towards the high-energy region for the hybrid functional. Additionally, the result of the total and projected DOS of the (CsMA)NaSbI₆ perovskite shows that the contribution to the total DOS towards VBM is by the Sb-5p states and I-5p states. The contribution to the total DOS towards CBM is by the I-5p states while the Na-3s states gave a partial contribution to the total DOS towards VBM. Moreover, it can be seen that the least contribution to the total DOS towards VBM is by the Na-3s states. This feature of the Na atom is also observed in the inorganic double perovskites, Cs₂NaBX₆(B = Bi, Sb; X = I,Br, Cl) investigated by [16]. The authors observed that although the Na atom is important to the formation of the double perovskite crystal, the Na s orbital is not involved in the composition of VBM.

### 3.3 Optical properties

The calculated dielectric functions, absorption coefficients, and real parts of the refractive indices of ANaBX₆ (A = CsMA, (MA)₂; B = Bi, Sb; X = Cl, Br, I) are presented in Fig. 5a–c.
The investigated optical properties of the considered hybrid double perovskites include the dielectric function, refractive index and the absorption coefficient. The dielectric function and refractive indices were observed for the photon energy from 0 to 30 eV while the absorption coefficients were observed for the wavelength from 0 to 800 nm. The (CsMA)NaSbI₆ perovskite has the highest dielectric constant at a higher energy region (2–4 eV) over the same energy region compared to the other hybrid double perovskites investigated.

Owing to the dependence of the absorptive behaviour of a material on the imaginary part of the dielectric function [16], the imaginary parts of the dielectric function of the considered compounds were investigated. The (CsMA)NaSbI₆ material depicts the highest value for the imaginary dielectric function of all the investigated compounds for solar radiation. This high value of the dielectric function of the (CsMA)NaSbI₆ material for solar radiation suggests that it is a potential optoelectronic material. Moreover, due to the dependence of photovoltaic performance of a material on a high dielectric constant or dielectric function at zero frequency, materials with large dielectric constant can hold a large amount of charge over a long period of time, thus enhancing the photovoltaic performance. Among the investigated hybrid double perovskites, the highest value of the dielectric constant is 4.43 obtained for the (CsMA)NaSbI₆ material. This value shows closeness to the dielectric constant of MAPbI₃ [11], with a value of 5.23. The discrepancy in value compared to the value of the dielectric constant for the (CsMA)NaSbI₆ material in the present study is 0.8. This closeness shows that other optical properties of the hybrid double perovskite (CsMA)NaSbI₆ material should be similar to those of the hybrid perovskite MAPbI₃.

The absorption coefficient of a material is a key determinant of its light harvesting capacity and plays a significant role in its application for solar energy conversion. The results showed that the investigated materials have high absorption coefficient with the highest absorption obtained with (CsMA)NaSbI₆. This suggests that the (CsMA)NaSbI₆ hybrid double perovskite would be a suitable substitute to Pb-based hybrid perovskites for solar cell applications. Additionally, the refractive index for (CsMA)NaSbI₆ in Fig. 5c showed the maximum peak (2.83) over a broad spectrum (2–4 eV). Thus, the (CsMA)NaSbI₆ material is suitable in optoelectronic applications such as liquid crystal display (LCD), organic light-emitting diode (OLED) and quantum dot light-emitting diode (QDLED) televisions, which require materials with high refractive index (>1.50) [2].

### 3.4 Thermal properties

Looking at Table 2, the calculated formation energies of the considered hybrid double perovskites are presented. The formation energy of a material is the change of enthalpy when 1 mol of a compound is formed from its constituents elements. As opined by [12], a negative formation energy of a material depicts the stability of the material. This stability increases with increasing negativity of the formation energy. As can be inferred from the results in Table 2, the formation energies of the I-based compounds show least negativity compared with that of Br or Cl-based compounds. In all, the results of the formation energies of the investigated compounds show that they are stable and can be utilized for different optoelectronic applications.
The first-principles study of (CsMA)NaSbX₆ (MA = methylammonium; X = Cl, Br, I) organic–inorganic hybrid double perovskites for optoelectronic applications is presented. The investigation of the structural, electronic and optical properties as well as the stability of three hybrid organic–inorganic double perovskites through the substitution of Cs with a combination of Cs and MA in the inorganic double perovskite, CsNaBX₆ (B = Sb; X = Cl, Br, I) based on first-principles DFT/LDA method shows that the electronic bandgap is largely dependent on the halogen content of the individual compound. This tunability of the material bandgap makes these compounds potential candidates for optoelectronic applications such as LEDs and lasers, among others. Moreover, of all the investigated materials in the present study, the (CsMA)NaSbI₆ hybrid organic–inorganic double perovskite depicts superior optical properties.

Fig. 5 The optical properties of double perovskites ANaBX₆ (A = CsMA, (MA)₂; B = Bi, Sb; X = Cl, Br, I) are along the incident electromagnetic radiation of energy from 0 to 30 eV. a Calculated dielectric function, b Calculated absorption coefficient, c Calculated refractive index

Table 2 Calculated formation energy, H (kJ/mol) of (CsMA) NaSbX₆ (X = Cl, Br, I)  
| Compounds               | H (kJ/mol) |
|-------------------------|------------|
| (CsMA)NaSbCl₆           | −5077.2    |
| (CsMA)NaSbBr₆           | −4909.8    |
| (CsMA)NaSbI₆            | −4667.4    |

4 Conclusion

The first-principles study of (CsMA)NaSbX₆ (MA = methylammonium; X = Cl, Br, I) organic–inorganic hybrid double perovskites for optoelectronic applications is
optoelectronic properties compared with the other compounds in the study as revealed by the LDA and HSE results with discrepancy in bandgap value of 0.20 eV due to the underestimation of the LDA method. Nonetheless, it has a high absorption coefficient and unique dielectric properties as well as a high refractive index compared to the other materials. In all, the hybrid organic–inorganic double perovskite (CsMA)NaSbI$_6$ has shown unique properties and, as such, could be a suitable candidate in the quest for Pb-free materials for optoelectronic applications.

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