First-Principles Study of (CsMA)NaSbX₆ (MA= Methylammonium; X=Cl, Br, I) Organic-Inorganic Hybrid Double Perovskites For Optoelectronic Applications

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Research Article

Keywords: Organic, Inorganic, Double, Perovskite, Optoelectronics

Posted Date: September 3rd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-842623/v1>

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Version of Record: A version of this preprint was published at Journal of Computational Electronics on January 6th, 2022. See the published version at <https://doi.org/10.1007/s10825-021-01832-2>.

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 than 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. 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 (in the order of 10⁶cm⁻¹), dielectric constant (approx.4.43), imaginary part of the 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.

Introduction

As the quest for new affordable and more efficient materials for use in optoelectronic applications such as photovoltaics is increasing, Materials Scientists are pushing the spheres 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 a good and stable substitute for photovoltaics (Roknuzzaman et al., 2019). 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 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, extended charge diffusion lengths with high lifetimes (Roknuzzaman, Ostrikov, Wang, Du, & Tesfamichael, 2017; Roknuzzaman et al., 2019).

Recently, great interest has been drawn to double perovskites with the basic formula A₂B'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⁻ (Kim & Kim, 2018; Sani & Shafie, 2019; Volonakis et al., 2016; Zhang, Liao, & Yang, 2019). This shift in focus is largely attributed to the fact that these materials offer suitable replacements for lead as well as the instability of lead-halide perovskites (Volonakis et al., 2016). Moreover, better optoelectronic properties have been observed for MA based organic –inorganic hybrid perovskites than Cs containing inorganic perovskites as well as the similarity in optoelectronic properties of Cs₂BiAgI₆ and Cs₂SbAgI₆ with MAPbI₃ (Roknuzzaman et al., 2019; Volonakis et al., 2016). Nonetheless, of all reviewed hybrid double perovskites (Filip, Filip, & Volonakis, 2018; Meng et al., 2017; Ogunniranye, Atsue, & Oyewande, 2020), 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 depletion of the copper ore (Rötzer & Schmidt, 2018) and the high cost of silver, the present work seeks to explore Na as a B" site element while investigating different combination to find 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) (Shuai & Ma, 2016; Volonakis et al., 2016). To curb cost associated with the precursors, CuCl, AgCl and AuCl required for the synthesis of inorganic double perovskites (Volonakis et al., 2016), from which hybrid organic-inorganic double perovskites are formed, this study posits the investigation of (CsMA)NaSbX₆ (X = Cl, Br, I) organic-inorganic hybrid double perovskites for optoelectronic applications by first principles DFT method.

Computational Method

The first-principles density functional theory (DFT) calculations have been performed using Quantum ESPRESSO (QE) package implemented in Materials Square (Lab, 2021). 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- Berke-Ernzerhof (PBE)(Ropo, Kokko, & Vitos, 2008). Moreover, to optimize the crystal structure and estimate the ground state energy, the Broyden-Fletcher-Gordfarb-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 all through the calculation, and to sample the Brillouin zone, the Monkhorst-Pack scheme k point of $4 \times 4 \times 4$ for obtaining the best convergence and total energy value was used. All investigated cells were fully relaxed until the cell stresses were at least $10^{-6} \text{ Ry/bohr}^3$ and the residual forces on each atomic site were at least 10^{-4} Ry/bohr .

Results And Discussion

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.

Table 1. Calculated lattice constants and bandgaps for hybrid double halide perovskites ANaBX₆ (A = CsMA, (MA)₂; B = Sb; X = Cl, Br, I).

Compounds	a (Å)	Bandgap (eV)
(CsMA)NaSbCl ₆	7.75	3.05
(CsMA)NaSbBr ₆	8.17	2.55
(CsMA)NaSbI ₆	8.77	2.09

From Table 1, it can be inferred that the bandgap energy increases with reducing lattice constants in accordance with the observation by (Greenman, Williams, & Kioupakis, 2019; Roknuzzaman et al., 2017) that the replacement of halogen atom (X) by a lighter and smaller halogen atom reduces the lattice parameter. Generally, the halogens increasing in atomic size down the group in Periodic Table (Kragh, 1963; Yao et al., 2021) and as such, increasing the halide concentration results in decrease of the bandgap energy.

Electronic properties

The electronic band structures for the hybrid double perovskite compounds are shown in Figs. 1–3. These hybrid double perovskites were predicted to be of indirect band gap as their inorganic double perovskites, Cs₂NaBX₆ (B = Bi, Sb; X = Cl, Br, I) (Shuai & Ma, 2016). The CBMs were shown to appear at the *X* point of the high symmetric path of the BZ with exception of (CsMA)NaSbI₆, with its CBM at the *R* point of the BZ. On the other hand, the VBMs of these materials were found to be at the *M* point. The calculated band gap values are presented in Table 1 from which it can be inferred that the iodide hybrid double perovskite ((CsMA)NaSbI₆ (2.09 eV)) exhibit the smallest band gap value. These value are comparable with that of Cs₂AgBiBr₆ (2.19 eV by measurement) (McClure, Ball, Windl, & Woodward, 2016). Moreover, all the perovskites in the present method gave band gap values of (CsMA)NaSbI₆ (2.09 eV), (CsMA)NaSbCl₆ (3.05 eV), (CsMA)NaSbBr₆ (2.55 eV). These values are comparable with that of (MA)₂BiAgCl₆ (2.7 eV) (Volonakis et al., 2016) within the same level of theory and MAPbCl₃ (3.0eV) (McClure et al., 2016) apart from, (CsMA)NaSbCl₆ (3.1 eV) in the present study which show slight deviations which could be attributed to its small value of lattice parameter as opined by (Greenman et al., 2019).

Moreover, the band gap of the investigated perovskites can be tuned by changing the halogen contents. This characteristic spurs usability in areas such as light emitting diode (LEDs) (Roknuzzaman et al., 2017, 2019).

In Figs. 4–6, the total and projected DOS of the considered hybrid double perovskites were calculated to investigate the band compositions of atomic orbital contribution towards electronic states at VBM and CBM. The result of the total and projected DOS of (CsMA)NaSbI₆ perovskite in Fig. 4. It is shown 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.

In Fig. 5, the total and projected DOS for (CsMA)NaSbCl₆ perovskite is shown from which it can be seen that the contribution to the total DOS towards VBM is by the Sb-5p states and Cl-3p states. The only contribution to the total DOS towards CBM is by the Cl-3p states. The Na-3s states is seen to contribute only partly to the total DOS towards VBM. For the (CsMA)NaSbBr₆ perovskite in Fig. 6, the main contribution to the total DOS towards VBM is by the Sb-5p states and Br-4p states. The Br-4p states is also seen to contribute to the total DOS towards CMB while the Na-3s states offers partial contribution to the total DOS towards VBM.

Looking at the results of the total and projected DOS in Figs. 4–6, it is evident that the halogen atoms contribute to the total DOS both towards VBM and CBM. This characteristic is pertinent to the observed change of band gap with the change of the halogen content in the hybrid double perovskites. Evidently for all the aforementioned hybrid double perovskites, 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 (Shuai & Ma, 2016). 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.

Optical properties

The calculated dielectric functions, absorption coefficients, real and imaginary parts of the refractive indices of ANaBX₆ (A = CsMA, (MA)₂; B = Bi, Sb; X = Cl, Br, I) are presented in Figs. 7–18.

The investigated optical properties of the considered hybrid double perovskites include, dielectric function, real and imaginary parts of the refractive index as well as 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 higher energy region (2–4 eV) function 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 (Shuai & Ma, 2016), the imaginary parts of the dielectric function of the considered compounds were investigated. The material (CsMA)NaSbI₆ 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 high dielectric constant or dielectric function at zero frequency, as materials with large dielectric constant can hold 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 of 4.43 is obtained for the (CsMA)NaSbI₆ material. This value shows closeness to the dielectric constant of MAPbI₃ (Roknuzzaman et al., 2017), with 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 ought to 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 posits 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. 8 showed the maximum peak (2.83) over a broad spectrum (2-4eV). Thus, the (CsMA)NaSbI₆ material can be suitable in optoelectronic applications such as liquid crystal display (LCDs), organic-light emitting diode (OLED), quantum dot light emitting diode (QDLED) televisions which require materials with high refractive index (>1.50) (Garner, 2019).

Thermal properties

Table 2. Calculated formation energy, H(kJ/mol) of of (CsMA)NaSbX₆ (X = Cl, Br, I)

Compounds	H(kJ/mol)
(CsMA)NaSbCl ₆	-5,077.2
(CsMA)NaSbBr ₆	-4,909.8
(CsMA)NaSbI ₆	-4,667.4

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 mole of a compound is formed from its constituents elements. As opined by (Roknuzzaman et al., 2019), 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.

Conclusion

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 3 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 = I, Br, Cl) based on first-principle DFT/LDA method shows that the electronic band

gap is largely dependent on the halogen content of the individual compound. This tunability of material band gap makes these compounds potential candidates for optoelectronic applications such as LED, laser among others. Moreover, of all the investigated materials in the present study, the (CsMA)NaSbI₆ hybrid organic-inorganic double perovskite depicts superior optoelectronic properties compared with the other compounds in the study. For instance, it has high absorption coefficient and unique dielectric properties as well as high refractive index compared to the other materials. In all, the hybrid organic-inorganic double perovskite (CsMA)NaSbI₆ has shown unique properties and as such, could be a suitable candidate in the quest for Pb-free materials for optoelectronic applications.

Declarations

Acknowledgement

The authors wish to acknowledge the Cloud Computing Interface of Materials Square and the Computational Facility of the Centre for Food Technology and Research (CEFTER), the World Bank Africa Centre of Excellence in Benue State University, Makurdi, Nigeria.

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Figures

Figure 1

Electronic band structure of (CsMA)NaSbI₆

Figure 2

Electronic band structure of (CsMA)NaSbCl₆

Figure 3

Electronic band structure of (CsMA)NaSbBr6

Figure 4

Total and projected density of states of (CsMA)NaSbI6.

Figure 5

Total and projected density of states of (CsMA)NaSbCl₆.

Figure 6

Total and projected density of states of (CsMA)NaSbBr₆.

Figure 7

Calculated dielectric function of (CsMA)NaSbI₆

Figure 8

Calculated real part of refractive index of (CsMA)NaSbI₆

Figure 9
 Calculated imaginary part of refractive index of (CsMA)NaSbI6

Figure 10
 Calculated absorption coefficient of (CsMA)NaSbI6

Figure 11

Calculated dielectric function of (CsMA)NaSbCl₆

Figure 12

Calculated real part refractive index of (CsMA)NaSbCl₆

Figure 13

Calculated imaginary part refractive index of $(\text{CsMA})\text{NaSbCl}_6$

Figure 14

Calculated absorption coefficient of $(\text{CsMA})\text{NaSbCl}_6$

Figure 15

Calculated dielectric function of (CsMA)NaSbBr₆

Figure 16

Calculated real part of refractive index of (CsMA)NaSbBr₆

Figure 17

Calculated imaginary part of refractive index of (CsMA)NaSbBr6

Figure 18

Calculated absorption coefficient of (CsMA)NaSbBr6