The study of electronic and optical properties of perovskites $CH_3NH_3PbCl_3$ and $CH_3NH_3PbBr_3$ using first-principle

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Abstract. At present, Organic-inorganic hybrid methylammonium lead halide perovskites $MAPbX_3$ (MA= CH_3NH_3; X = Cl, Br) have recently attract attention scientific researchers, as a promising candidate for photovoltaic and optoelectronic devices. We have studied the electronic structures and optical properties of perovskites $CH_3NH_3PbBr_3$ and $CH_3NH_3PbCl_3$, using density functional theory (DFT). These physical properties are calculated by CASTEP code, such as the band structures, total density of states (TDOS), absorption coefficient, refractive index and optical conductivity. The analysis of band gap shows that these two perovskites are semiconducting materials. Calculated absorption coefficient of $CH_3NH_3PbBr_3$ and $CH_3NH_3PbCl_3$ shows an absorption peak around 3.87 eV and 2.04 eV, respectively. The above results provide good agreement with experimental work for optoelectronic properties of $CH_3NH_3PbBr_3$ and $CH_3NH_3PbCl_3$ materials.

1. Introduction

Hybrid perovskites have drawn attention of researchers in the field of photovoltaics by their potential in high efficiency solar cells [1,2]. The perovskites combine an easy and inexpensive manufacture with excellent optoelectronic properties [3]. The electronic and optical characteristics of two organic/inorganic hybrid lead-halide perovskites MAPbX3 (MA= CH3NH3; X= Br, Cl) were calculated using the CASTEP code. The CASTEP programme can simulate the physical characteristics of these two perovskites, including electrical and optical properties, using the functional theory of density.

The generalized gradient approximation (GGA) parameterized by Wu-Cohen (WC), was used to optimize the network parameters, and determined the band gap, TDOS, absorption coefficient, dielectric function, refractive index and optical conductivity, in the energy range 0-6 eV.

We assume the orthorhombic structure of $MAPbBr_3$ with Pnma symmetry and the lattice parameters (a = 8.547 Å, b=12.183Å, c=8.421Å, α=β=γ=90°), at room temperature. The structure of $MAPbCl_3$ is tetragonal with P1 symmetry (a=b=8.217926Å, c=12.349893Å, α=β=γ=90°). The structures of these two perovskites are fully optimized by the total minimization of energy, and are represented in Fig.1 and Fig.2.

The $MAPbCl_3$ and $MAPbBr_3$ perovskites, are investigated as a transparent semiconductor. These compounds are found to be direct band gap semiconductors suitable for solar cells, and several optoelectronic devices. The results obtained by first-principles calculations using generalized gradient approximation (GGA), are in good agreement with the experimental results [4-5-6].

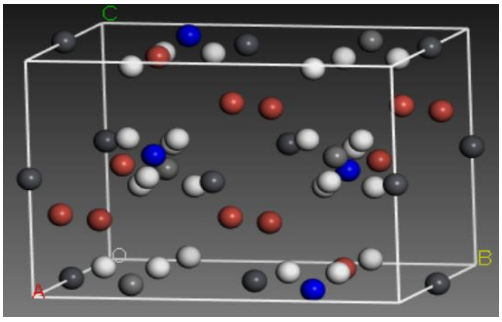

Fig. 1. The structure of $CH_3NH_3PbBr_3$, the color cod: white (H), light gray (C), blue (N), dark gray (Pb) and dark brown (Br).

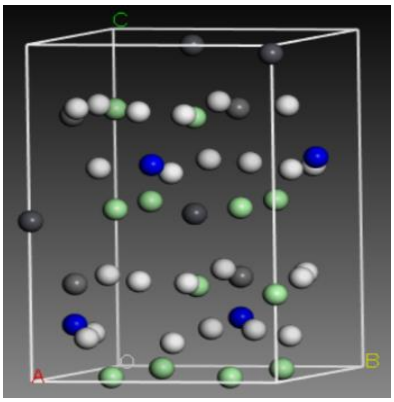

Fig. 2. The structure of $CH_3NH_3PbCl_3$, the color cod: white (H), light gray (C), blue (N), dark gray (Pb) and green (Cl).

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2. Results and discussion

2.1 Electronic properties

2.1.1 Band gap

The band gap, is a range of energy in a solid, where no electronic state can exist. It is the energy between the maximum valence band and the minimum conduction band. Fig.3 and Fig.4 shows the electronic band structure of $MAPbBr_3$ and $MAPbCl_3$ perovskites. The GGA approach was used to calculate the bandgap of $MAPbBr_3$ and $MAPbCl_3$ to increase the precision of the bandgap calculation of these compounds to its maximum. The bandgaps obtained from the GGA-PBE approach for $MAPbBr_3$ and $MAPbCl_3$ are 2.415 eV and 2.402 eV respectively, indicating that MAPbBr3 and MAPbCl3 are direct bandgap semiconductor materials. These values are compared with other theoretical and experimental results in Table 1, as can be seen, the results of the GGA approach are very consistent with the experimental data [7-8-9-10].

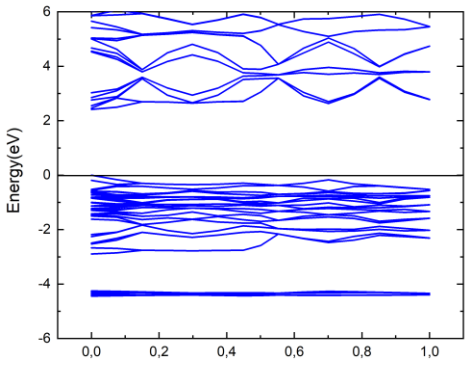

Fig.3. Calculated band-structure of $MAPbBr_3$ perovskite.

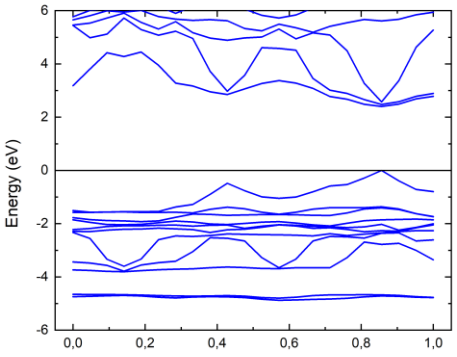

Fig. 4. Calculated band-structure of $MAPbCl_3$ perovskite.

Table 1. The calculated band gaps of $MAPbX_3$ (X= Br, Cl) for GGA-PBE, PBEsol approach beside experimental reports.

Samples	GGA-PBE	PBEsol	Exp
$MAPbBr_3$	2.415 eV	1.82 eV	2,3 eV
$MAPbCl_3$	2,402 eV	2.27 eV	2,94 eV

2.1.2 Total density of states

In solid state physics, the TDOS quantifies the number of electronic states likely to be occupied, and having a given energy in the material considered. The Fig.5 and Fig.6 are represented the total density of states of $MAPbBr_3$ and $MAPbCl_3$ perovskites, respectively, calculated by using the GGA-PBE approximation. The TDOS profiles show the positions of characteristic peaks and the participation of individual electronic states of C, N, H, Pb, Cl and Br atoms which interact with each other to form perovskites systems. The computed TDOS spectra show the distinct regions composed of valence bands and a region containing the conduction band. Note that the separation between the upper part of the valence states and the lower region of the conduction states illustrates the band gap, this implies that the two perovskites structures $MAPbCl_3$ and $MAPbBr_3$ exhibit semiconductor behavior.

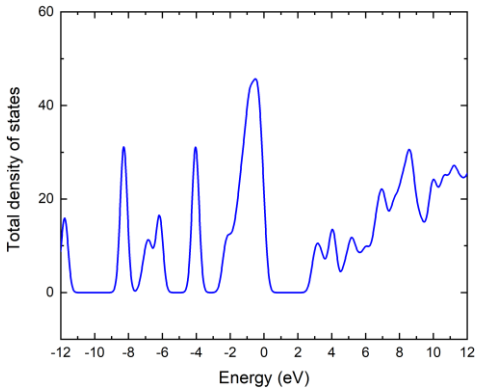

Fig. 5. Calculated TDOS of $MAPbCl_3$ perovskite

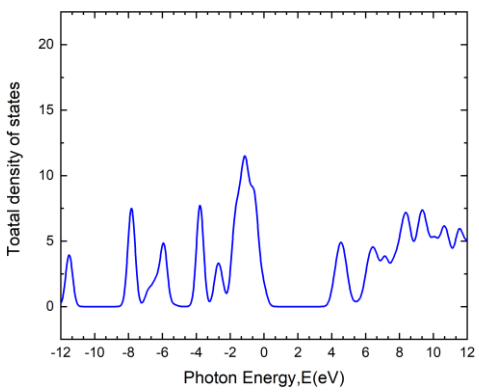

Fig. 6. Calculated TDOS of $MAPbBr_3$ perovskite.

2.2 Optical properties

2.2.1 *Dielectric function*

Properties of crystalline solids can be described by the dielectric function:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (1)$$

Where $\varepsilon_1(\omega)$ and $\varepsilon_1(\omega)$ are the dielectric function's real and imaginary parts, respectively. The Kramers-Kronig relations [11] can be used to derive the real component of the dielectric function from the imaginary part of the dielectric function. The imaginary part of the dielectric function is very important to calculate the optical constants of materials [12]. The imaginary part of the dielectric function, can be calculated from the elements of the momentum matrix, related to the occupied and unoccupied wave functions according to the selection rules [11], it can be calculated using the relation:

$$\varepsilon_2(\omega) = \frac{2\pi e^2}{\Omega \varepsilon_0} \sum_{k,v,c} |\langle \phi_k^c | \boldsymbol{u}.\boldsymbol{r} | \phi_k^v \rangle|^2 \, \delta\left(E_k^c - E_k^{\vartheta v} - E\right) \quad (2)$$

In this relation ω represented de photon energy, e is the electronic charge, Ω is the volume of unit cell, ϕ_k^c and ϕ_k^v they are the waves functions, respectively, for the electron of conduction band and valence band, for a particular k and $\boldsymbol{u}$ is the unit vector along the polarization of the incident electric field, and $\langle \phi_k^v \rangle$ represent the components of the dipole moment matrix .

The response of a material to incident solar radiation is characterized by the dielectric function. The static dielectric constant (dielectric function for zero photon energy) is an important material indicator for optoelectronic applications since a high dielectric constant increases overall device performance and reduces charge carrier recombination [13]. Figures 7 and 8 show the variation of the real and imaginary parts of the dielectric function as a function of frequency, respectively.

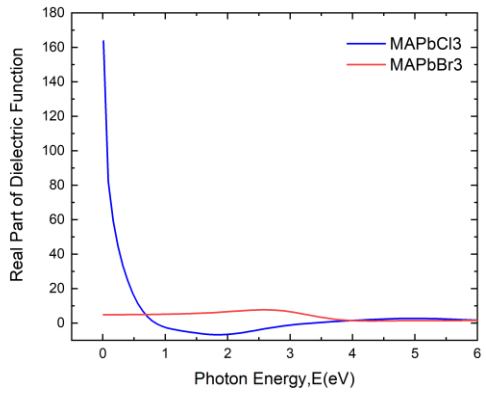

Fig. 7. Calculated the real part of the dielectric function of perovskites $MAPbX_3$ (X = Cl, Br) as a function of frequency.

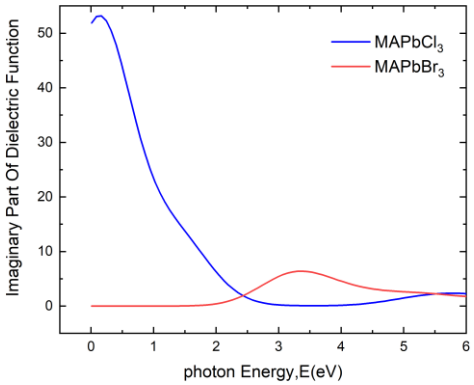

Fig. 8. Calculated imaginary part of the dielectric function of perovskites $MAPbX_3$ (X = Cl, Br) as a function of frequency

We find that the $MAPbCl_3$ material, characterized by the band gap energy E_g= 2.402 eV at a maximum dielectric constant value 164.08, and the $MAPbBr_3$ perovskite characterized by E_g= 2.515 eV at a maximum dielectric value 4.94. Therefore, it is clear that when the energy of the band gap increases, the dielectric function decreases. Consequently, the $MAPbCl_3$ material is a better candidate than $MAPbBr_3$ in terms of dielectric constant. The amplitude of the real and imaginary parts of the dielectric function decreases, due to the replacement of Cl by Br. The imaginary part of the two perovskites tends towards zero, when the energy of the photon increases [14].

2.2.2 *Refractive index*

In semiconductors, the refractive index characterizes the measure of the transparency of the material to incident photons, it is a dimensionless number that describes the speed at which light passes through the material. The real part of the complex refractive index of a material is described by the refractive index $n(\omega)$ by the following formula.

$$n(\omega) = \sqrt{\frac{\varepsilon_1(\omega)}{2} + \sqrt{\frac{(\varepsilon_1(\omega))^2 + (\varepsilon_2(\omega))^2}{2}}} \quad (3)$$

To measure the transparency of the $MAPbCl_3$ and $MAPbBr_3$ systems to incident light. The refraction spectra $n(\omega)$ are shown in Fig. 9.

It appears that the refractive index, n does not reveal the significant alteration of the energies of the photons upward the band gap energy, which means that these materials demonstrate optical stability. The static refractive index, n(0) is a valuable physical quantity for semiconductors. The value of the static refractive index n(0) for $MAPbBr_3$ is approximately 2.21.

The deviations of the refractive index come from the morphology, the chemical composition, the anisotropy and the differences in layer thickness of the $MAPbBr_3$ films. Also, the refractive index of $MAPbBr_3$ is included between 2.2 and 2.82, and increases in the energy range [0- 2.8 eV]. Its maximun

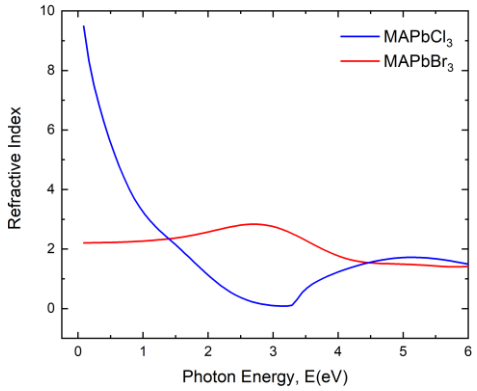

Fig. 9. Calculated refractive index of perovskites $MAPbX_3$ (X=Cl, Br) as a function of frequency.

value is n = 2.32 at energy E = 2.8 eV, and decreases in the energy range [2.8 eV- 6 eV]. Even the value of the static refractive index of $MAPbCl_3$ is about n(0) = 9.48. The refractive index of $MAPbCl_3$ decreases, by reason of the increases of the energy. But, when the energy of the incident photon reaches the value E = 3.28eV, the refractive index increases and reaches the maximum value n = 1.72. From the analysis of the refraction spectrum of the two structures $MAPbBr_3$ and $MAPbCl_3$, it appears that these materials have different refraction indices. These results found are in good agreement with the experience.

2.2.3 *Absorption coefficient*

The absorption coefficient is a very important optical property for energetic materials and solar cells, it gives us more important information concerning the penetration of light of a specific wavelength (well determined energy) before the light gets absorbed and efficiency optimal solar energy conversion. The sun emits light at different frequencies, in the form of photons. The energy of the photon depends on its wavelength λ.

$$E_{photon} = h.\vartheta = \frac{h.c}{\lambda} \quad (4)$$

In this equation, h is the Planck's constant, c is the speed of light in vacuum and ϑ is the frequency.

Two factors determine whether or not the photon is absorbed by the material. The first factor is the width of the band gap of the semiconductor (E_g). We can have three different situations:

1- If $E_{photon} < E_g$, the photon is not absorbed.

2- If $E_{photon} = E_g$, the photon is absorbed by the semiconductor.

3- If $E_{photon} > E_g$, the photon is absorbed by the semiconductor, but the relaxation in the bands towards the electronic states near the gap causes a loss energy.

The absorption of a material is described by the formula.

$$\alpha(\omega) = 2\omega\sqrt{\frac{-\varepsilon_1(\omega)}{2} + \sqrt{\frac{(\varepsilon_1(\omega))^2+(\varepsilon_2(\omega))^2}{2}}} \quad (5)$$

The perovskite $MAPbBr_3$ has two peaks in ultraviolet range, these two peaks are more important of solar cells, because it resides in the energy of solar radiation (2 to 6 eV). The first peak corresponds to an absorption coefficient $4{,}4.10^4 cm^{-1}$ at energy $E =$ 3.89 eV. The second peak corresponds to an absorption coefficient $7{,}03.10^4\ cm^{-1}$ at energy $E = 5.4\ eV$. The perovskite $MAPbCl_3$ has a single peak observed in visible domain, its intensity is $8{,}92.10^4\ cm^{-1}$ at energy $E = 2.038\ eV$.

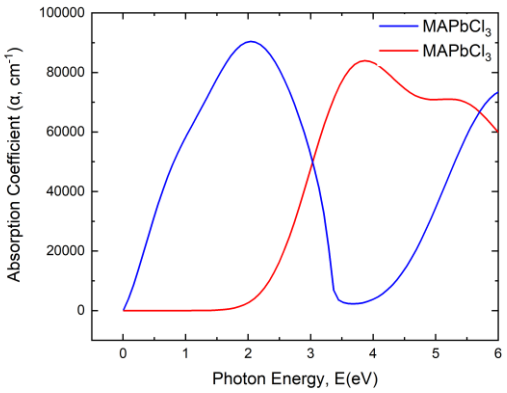

Fig. 10. Calculated the absorption coefficient as a function of frequency of $MAPbCl_3$ and $MAPbBr_3$ perovskites.

2.2.4 *Optical Conductivity*

Optical conductivity is a property of the material which gives the relationship between the current density induced in the material and the amplitude of the inducing electric field for arbitrary frequencies. Fig. 11 represents the optical conductivity of the two perovskites $MAPbCl_3$ and $MAPbBr_3$. It is clear that the change in optical conductivity of the two perovskites is almost similar to the change in absorption coefficient. Here, the $MAPbCl_3$ perovskite start to lead to low energy and has a maximum conductivity σ =2.93 1/fs at energy E= 0.75 eV. So, this material conducts in low energy, this is a possible reason for a higher PCE for $MAPbCl_3$. However, the MAPbBr3 compound only begins to lead from the energy E= 2 eV and also has a maximum conductivity σ= 2.64 1/fs at the energy of the incident photon E= 3.84 eV. The optical conductivity of the two perovskites is considered to be similar for solar radiation. Thus, these results indicate the $MAPbCl_3$ and $MAPbBr_3$ materials are the good candidate for the applications in solar cells and many optoelectronic devices.

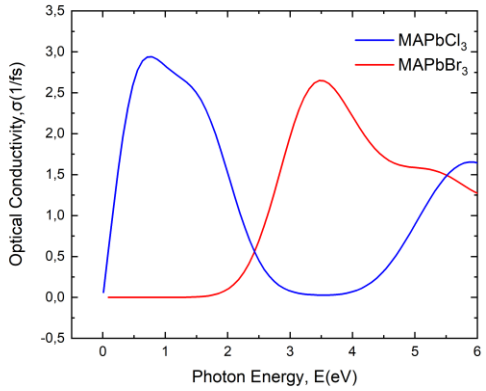

Fig. 11. Calculated the optical conductivity as a function of frequency of $MAPbCl_3$ and $MAPbBr_3$ perovskites.

3. Conclusion

The electronic and optical properties of the hybrid perovskites $FAPbBr_3$ and $MAPbCl_3$, are calculated using CASTEP code. The real and imaginary parts of dielectric functions, optical absorption spectra, refractive index and optical conductivity, were calculated on the photonic energy range 0 - 6 eV. It is important to note that the perovskites with the halides $MAPbBr_3$ and $MAPbCl_3$ are very promising systems of photovoltaic applications, because their optical absorption spectra cover the visible and ultraviolet regimes. Interestingly, these hybrid organic and inorganic perovskite solar cells have become one of the most exciting photovoltaic technologies. Based on these systems, it is possible to manufacture light harvesting materials for solar cells.

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