

Theoretical investigations on the electronic and optical properties of Na-doped $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite

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Abstract. The development of important materials for photovoltaic applications is rapidly advancing, particularly in the field of perovskite materials. This study investigates the optical and electronic characteristics of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and analyzes the influence of doping in perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ with different concentrations of sodium ions Na^+ . In this study, we employed Density Functional Theory to assess the optical and electronic properties of both pure and Na^+ ion-doped $\text{CH}_3\text{NH}_3\text{PbI}_3$, with Na^+ concentrations of 12.5 %, 25 %, and 37.5 %. The bandgap energy of pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ rises from 1.205 eV to 1.573 eV as the concentration of Na^+ ions increases from 0 % to 37.5 %, respectively. Doping with Na^+ ions leads to an increase in the absorption coefficient of pristine $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite in both UV and visible ranges. Doping likewise affects the density of states, dielectric function, and the refractive index of $\text{CH}_3\text{NH}_3\text{PbI}_3$ material. These findings offer vital insights into modulating the electronic and optical characteristics of $\text{CH}_3\text{NH}_3\text{PbI}_3$ through Na^+ ion doping.

Key word: Perovskite, $\text{CH}_3\text{NH}_3\text{PbI}_3$, TDOS, refractive index

1. Introduction

The consumption of energy becomes greater due to the increase in world population and also the increase in industry units which increases the problem of energy shortage and also the pollution of the environment, therefore it is necessary and urgent to find a new renewable and non-polluting energy, solar energy has become one of its first choices [1–3]. Photovoltaic energy is a non-polluting renewable energy, which relies on solar cells for the

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deflection of light rays, new research is being carried out around metal halide perovskites of formula ABX_3 [4,5], where A^{+} represents organic ion $CH_3NH_3^+$ (MA^+), B^{2+} represent Pb^{2+} , and X^{-} is a halide anion (Cl^{-} , Br^{-} or I^{-}) because these perovskites have very important optical and electronic properties in the field of solar energies. In 2009, Kojima and Coll integrated 3D perovskite $MAPbI_3$ into solar cells with liquid electrolyte, they obtained the efficiency of 3.8 %. In 2012, other research on perovskite was carried out by replacing the liquid electrolyte with a solid electrolyte which achieves the efficiency 9 %. Our study is based on the study of the electronic and optical properties of methylammonium lead triiodide perovskite of general formula $CH_3NH_3PbI_3$.

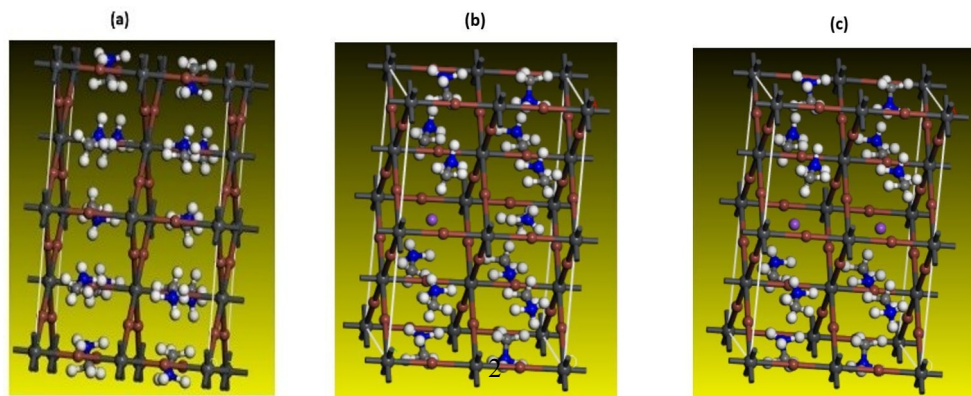
During the last years, $MAPbI_3$ perovskite has been widely used as an absorption layer in the field of solar energy, because of its most important advantages which are manifested by a large absorption coefficient, an appropriate bandgap energy, high photoelectric conversion efficiency and superior photoelectric properties [6, 7]. $MAPbI_3$ Perovskite has three crystal structures, which are orthorhombic, tetragonal and cubic. An orthorhombic structure for a temperature below 162.2 K with a space group of P221, a tetragonal structure at a temperature between 162 K and 327.4 K of space group I4/mcm and a cubic structure at a temperature above 327.4 K with Pm3m space group.

In this work we studied the optoelectronic properties of pure perovskite $MAPbI_3$ and also the effect of different sodium ions Na^+ doping on the optoelectronic properties. We doped the $CH_3NH_3^+$ cation by the Na^+ ions with the 12.5 % Na^+ , 25 % Na^+ and 37.5% Na^+ .

2. Computational methods

Electronic and optical properties of $CH_3NH_3PbI_3$ perovskite are determined by the DFT calculations. These properties are calculated by using the Cambridge Sequential Total Energy Package (CASTEP) [8, 9]. The valence electrons in the $CH_3NH_3PbI_3$ structure were represented using ultrasoft pseudopotentials to ensure high precision by the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) [10-12]. The OTFG Ultrasoft pseudo-potential was utilized to describe the interaction between electrons and ions [13-14]. The optimization geometry of the materials is important to obtain stable states of the relaxed structures, which means that strict convergence criteria must be verified in the relaxation of the positions of the atoms and also for the lattice parameters. A plane-wave energy cut-off of system was set to 400 eV for all calculations.

The K points of the Brillouin zone was sampled using $4 \times 4 \times 1$. In the self-consistent field operation, the Pulay density mixing method is adopted in the self-consistent field operation



and the self-consistent field is set to eV/atom [15]. The maximum stress was set to 0.1 GPa. The valence of electrons involved in the calculation are H: $1s^1$, C (Carbon): $2s^2 2p^2$, N (Nitrogen): $2s^2 2p^3$, Na (Sodium): $3s^1$, Pb (Lead): $6p^2$, I (Iodine): $5s^2 5p^5$, respectively. The $2 \times 1 \times 1$ supercell of $MAPbI_3$ of tetragonal structure at normal temperature with the lattice parameters $a = b = 8.851 \text{ \AA}$, $c = 8.12.444 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$ has been studied in this work. The Fig. 1 represents the tetragonal structure of the perovskite $MAPbI_3$ and the structures doped with sodium.

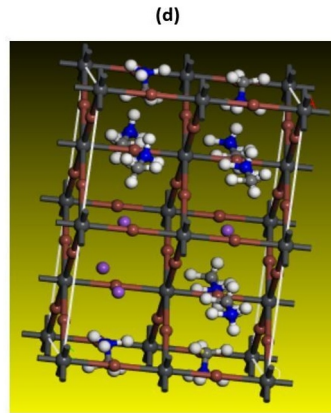


Fig.1. The tetragonal structure of pure and doped $CH_3NH_3PbI_3$, (a) pure structure, (b) $MA_{0.85}Na_{0.125}PbI_3$ structure, (c) $MA_{0.75}Na_{0.25}PbI_3$ structure (d) $MA_{0.625}Na_{0.375}PbI_3$, the color cod: white (H), Black (C), blue (N), bluish-gray (Pb), purple (Na) and dark gray (I).

3. Results and discussions

3.1 Electronic structure

3.1.1 Band gap

The photovoltaic conversion efficiency of solar cells is related to the photoelectric property and the band structure of material. The bandgap energy of $MAPbI_3$, $MA_{0.85}Na_{0.125}PbI_3$, $MA_{0.75}Na_{0.25}PbI_3$ and $MA_{0.625}Na_{0.375}PbI_3$ were calculated along high symmetry directions in the Brillouin zone, and graphically presented in Fig. 2. The computed bandgap energy of the $MAPbI_3$ structure reveals that the perovskite $MAPbI_3$ is a semiconductor with a direct bandgap [16]. The bandgap energy of pure $MAPbI_3$ and doped structures $MA_{0.85}Na_{0.125}PbI_3$, $MA_{0.75}Na_{0.25}PbI_3$ and $MA_{0.625}Na_{0.375}PbI_3$ are 1.205 eV, 1.512 eV, 1.559 eV and 1.573 eV, respectively. This demonstrates that these structures are semiconductor materials. The conduction band's minimum and the valence band's maximum both reside at point G within the Brillouin zone. These results suggest that doping MA^{+} cation by different concentrations of Na^{+} increased the direct bandgap of the $MAPbI_3$ semiconductor. Doping of Na^{+} ions will result in an disturbance of the

electrical equilibrium within MAPbI_3 . The positive charges carried by Na^+ ions will generate repulsive forces against the positive charges of $\text{CH}_3\text{NH}_3^{+}$ ions and lead ions, consequently giving rise to the generation of charge defects.

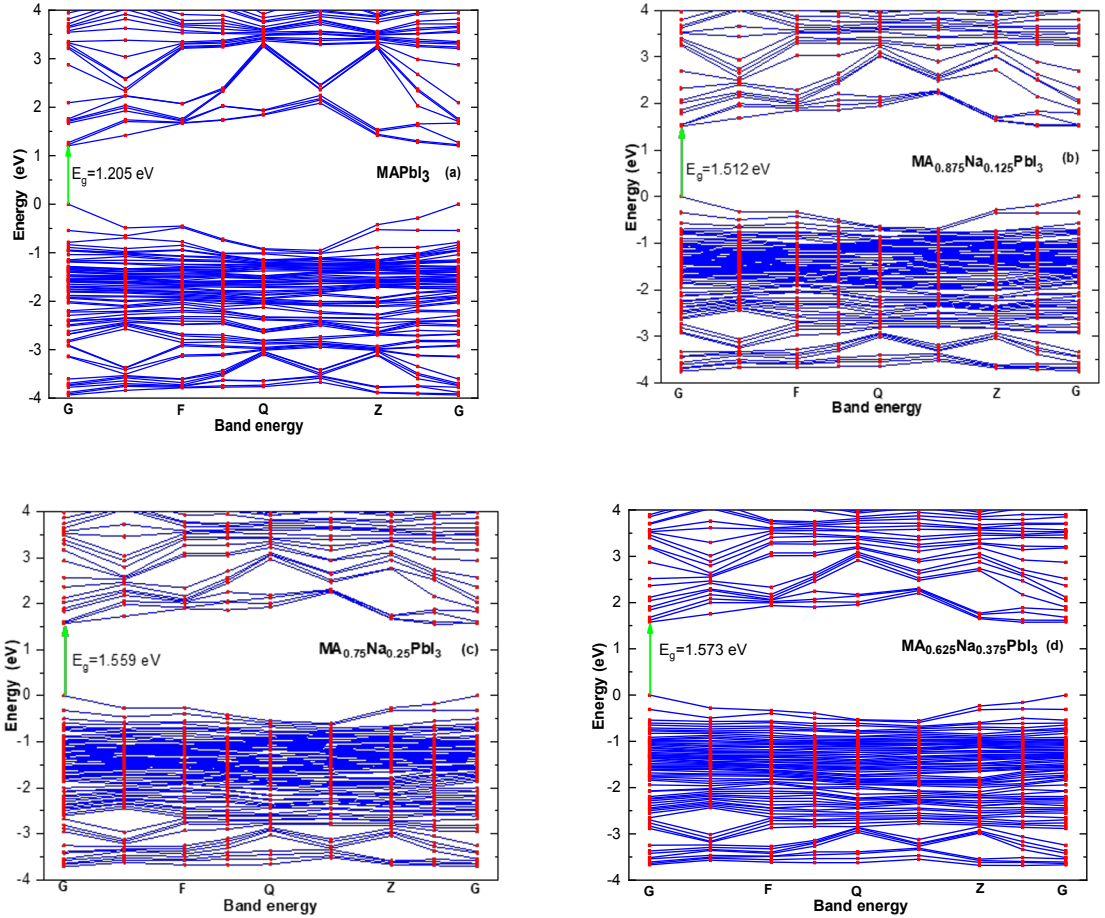


Fig. 2. Band structure of the tetragonal structure of pure and doped $\text{CH}_3\text{NH}_3\text{PbI}_3$, (a) pure structure, (b) $\text{MA}_{0.85}\text{Na}_{0.125}\text{PbI}_3$ structure, (c) $\text{MA}_{0.75}\text{Na}_{0.25}\text{PbI}_3$ structure (d) $\text{MA}_{0.625}\text{Na}_{0.375}\text{PbI}_3$.

3.1.2 Total density of states

The nature of bandgap energies is ascertained through the total density of states (TDOS), which displays the distribution of Kohn-Sham eigenvalues for different occupied and unoccupied orbitals. The gap between the upper valence states and the lower conduction states signifies the bandgap energy. In Fig. 3, the TDOS is illustrated for both undoped

MAPbI₃ and MAPbI₃ doped with Na⁺ ions. These calculations were performed using the GGA-PBE approximation. The profiles of the TDOS reveal the locations of distinctive peaks and the involvement of individual electronic states associated with H, C, N, Pb, I, and Na atoms. These states interact with one another to create perovskite systems. The calculated TDOS spectra reveal separate regions comprising the valence bands and a region encompassing the conduction band. It's clear that doping of Na⁺ ions has a negligible influence on the TDOS shape and the intensity of peaks of the CH₃NH₃PbI₃ material.

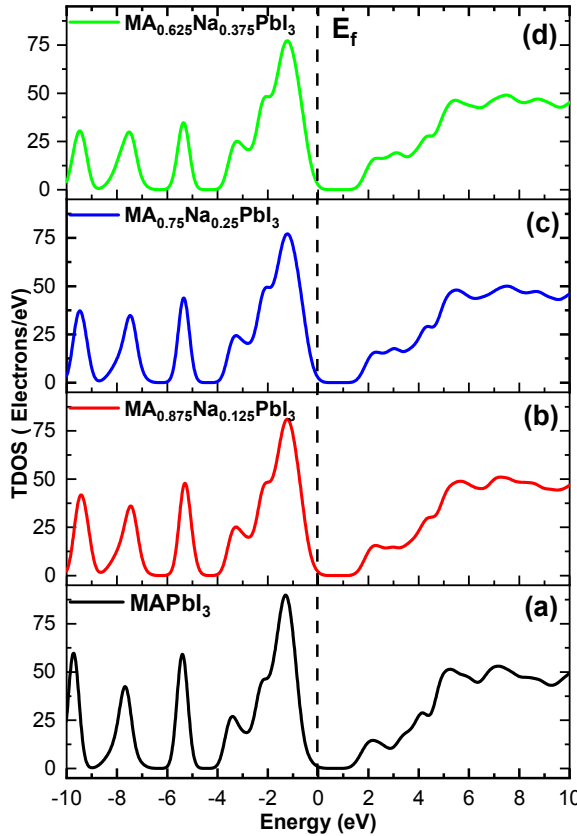


Fig. 3. TDOS of pure structure and $MA_{1-x}Na_xPbI_3$ structure, doping ration ($x = 0.125, 0.25, 0.375$).

3.2 Optical properties

3.2.1 Absorption coefficient

The absorption coefficient is a vital optical property for solar cells and materials used in energy-related applications. It provides information about the material's ability to allow light of a specific wavelength to penetrate and be absorbed, thereby influencing its efficiency in converting solar energy. The spectral absorption coefficient of the $MA_{1-x}Na_xPbI_3$ ($x = 0.125, 0.25, 0.375$)

perovskite is depicted in Fig. 4, revealing an absorption peak within the range of 350 nm to 400 nm. In the case of the pure structure, the peak absorption occurs at around 380 nm, falling in both UV and visible regions. As the concentration of sodium ions in the doping process increases, the absorption coefficient peak increases and shifts towards a lower wavelength. This shift enhances the material's ability to efficiently absorb the ultraviolet light. These findings suggest that MAPbI₃ system with partial Na⁺ doping are more suitable for absorbing UV light.

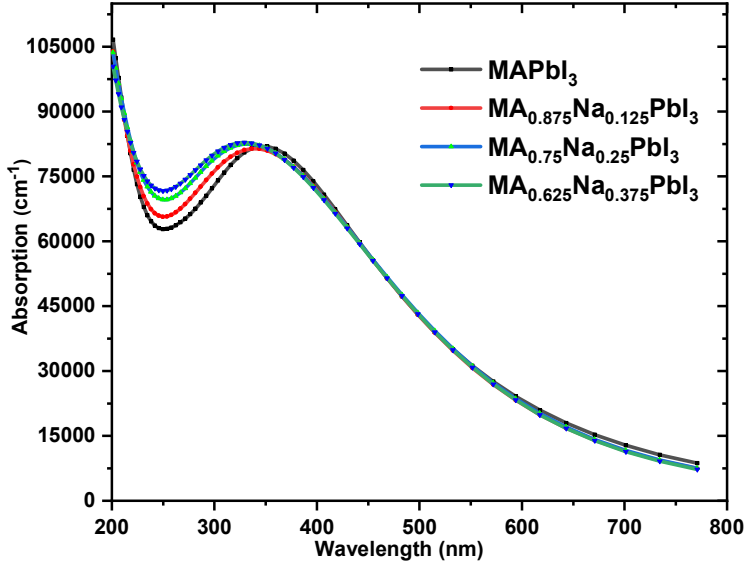


Fig. 4. Calculated absorption coefficients of pure $MA Pb I_3$ and doped structures $MA_{1-x} Na_x Pb I_3$ ($x = 0.125, 0.25, 0.375$) as a function of wavelength.

3.2.2 Dielectric function

The dielectric function, $\epsilon(\omega)$, is a physical parameter that describes the interaction of light with a substance when it traverses through a material. By employing the dielectric function, one can reveal the properties of crystalline solids. $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ express the actual and imaginary parts of the dielectric function, respectively. The real component quantifies a material's capacity to retain electrical energy in the presence of an electric field, impacting polarization and various electrical and electromagnetic applications. Meanwhile, the imaginary part indicates energy dissipation in the form of heat when a material experiences an alternating electric field, which is significant in the context of dielectric absorption [16]:

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) = \frac{16\pi}{N_k \Omega} \sum_{k,v,c} \frac{|\langle \phi_{kv}^{rel} | \tilde{V} | \phi_{kc}^{rel} \rangle|^2}{(\tilde{E}_{kc}^{GW} - \tilde{E}_{kv}^{GW})^2 (\tilde{E}_{kc}^{GW} - \tilde{E}_{kv}^{GW} - \omega - i\eta)} \quad (1)$$

The parameter N_k indicates the total number of k-points in the Brillouin zone.

Ω : is the volume of unit cell.

$\tilde{V}$: is the velocity operator.

$\hbar$: is an opportune broadening factor.

ϕ_{kc}^{rel} and ϕ_{kv}^{rel} represent occupied and unoccupied state wave functions at the k points in reciprocal space, respectively. Furthermore, the real component of the dielectric function can be inferred based on the imaginary component of the dielectric function, as prescribed by the Kramer-Kronig formula [17].

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'$$

(2)

Our objective is to assess the dielectric function of both pure MAPbI₃ and MAPbI₃ doped with Na⁺ ions at various concentrations, across a range of wavelengths (λ) spanning from 200 to 1400 nm, as illustrated in Fig. 5. The intensity of the peak in the real component of the dielectric function rises within the visible range and diminishes in the ultraviolet region as the concentration of Na⁺ ions increases from 0 % to 37.5 %. These results due to the electronic transitions. $\varepsilon_1(\omega)$ part decreases beyond 800 nm because the energy of the photons becomes insufficient to excite the electrons (see Fig. 5 (a)). The rise in the imaginary part of the dielectric function in the UV range is a result of the heightened absorption of photons within this wavelength range. After $\lambda = 800$ nm of incident photons, there is a decline in photon energy, leading to a reduction in electronic absorption and the imaginary component of the dielectric function in the MAPbI₃ structure due to the doping effect with Na⁺ (see Fig. 5 (b)).

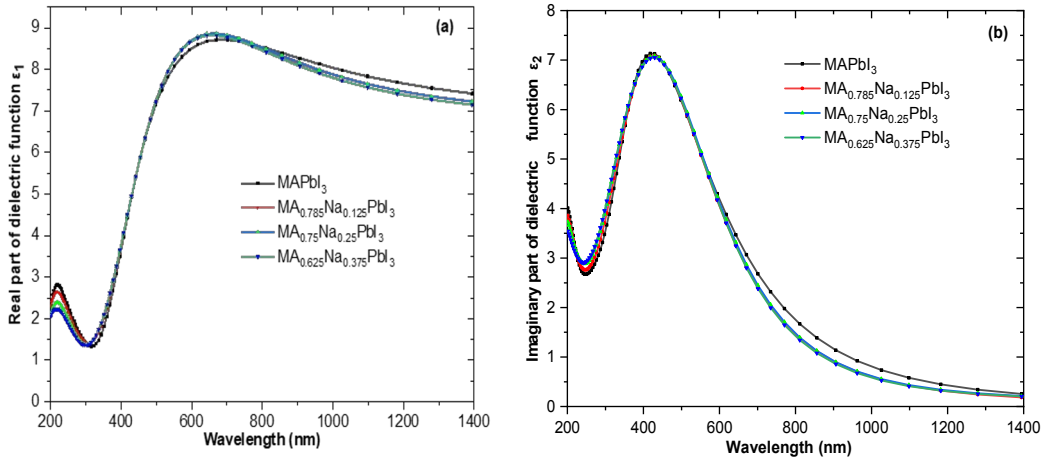


Fig. 5. Real and imaginary part of dielectric function of pure structure $MAPbI_3$ and doped structure $MA_{1-x}Na_xPbI_3$ ($x = 0.125, 0.25, 0.375$) as a function of wavelength.

3.2.2 Refractive index

The capacity of a substance to allow light to pass through it is quantified by its refractive index, a dimensionless figure that signifies the velocity of light within the material. The

subsequent equation can be employed to compute the actual component of the complex refractive index, denoted as [18,19]:

$$n(\omega)=\sqrt{\frac{\epsilon_1(\omega)}{2}+\sqrt{\left(\epsilon_{\text{imag}}^1(\omega)\right)^2+\frac{\left(\epsilon_{\text{imag}}^2(\omega)\right)^2}{2}}}$$

(3)

In order to assess how transparent both the pure $MAPbI_3$ and the Na-doped structure are to light, measurements were performed to evaluate their reaction when exposed to incoming light. The CASTEP software was utilized to calculate the alterations in the refractive index for both pure MAPbI₃ and MAPbI₃ doped with Na⁺ ions across various wavelengths of incident photons from 200 to 1800 nm, as depicted in Fig. 6. The introduction of Na⁺ ions into the MAPbI₃ system results in an augmentation of the refractive index within the visible spectrum and a reduction in the ultraviolet range. This phenomenon is attributable to the interaction between photons and electrons, as well as the scattering of light within the MAPbI₃ material.

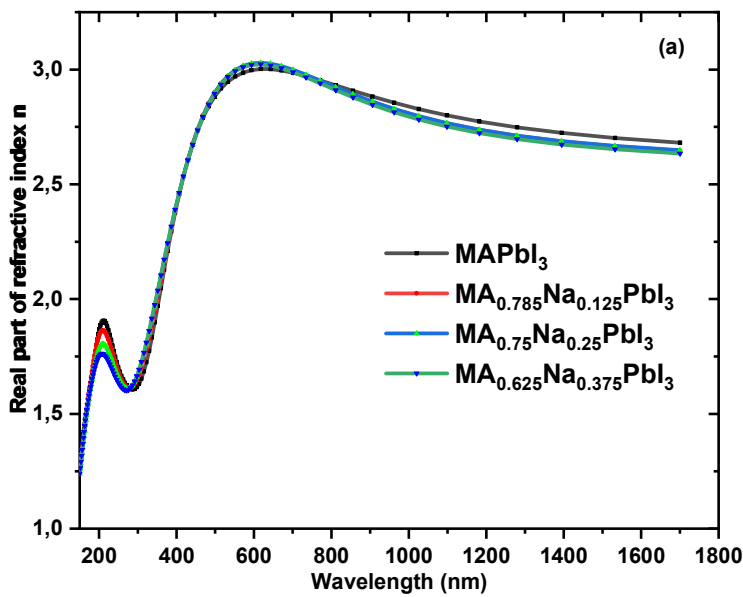


Fig. 6. Refractive index of pure structure $MAPbI_3$ and doped structure $MA_{1-x}Na_xPbI_3$ ($x = 0.125, 0.25, 0.375$) as a function of wavelength.

4. Conclusion

In this paper, we have investigated the electronic, and optical characteristics of both pristine MAPbI₃ and doped with varying concentrations of Na⁺ ions. This study was carried out through first-principle calculations employing the DFT method. Throughout the entire analysis, we applied the GGA+PBE approximation, which is integrated into the CASTEP software. The introduction of sodium Na⁺ doping at concentrations of 12.5 %, 25 %, and 37.5 % in the pristine CH₃NH₃PbI₃ perovskite led to a gradual increase of the bandgap energy and an enhancement of the absorption coefficient in the ultraviolet range. Na⁺ doping had minimal impact on the overall density of states, refractive index, and dielectric function of CH₃NH₃PbI₃. These findings hold significant potential for enhancing the electronic and optical characteristics of this material in a range of applications, such as photovoltaic cells and light-emitting devices.

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