Advancing optoelectronics: Exploring the superior performance of lead-free halide perovskites

Hamza Kerrai[1], Ahmed Zaim[1], Mohamed Kerouad[1]

1: Physics of Materials and Systems Modeling Laboratory, Moulay Ismail University, Faculty of Sciences, Meknes, Morocco

Abstract: In our study, we thoroughly examined the structural, electronic, and optical properties of halide double perovskites $Cs_2AgSb(Cl,Br)_6$ using density functional theory. The band structure analysis revealed that $Cs_2AgSbCl_6$ and $Cs_2AgSbBr_6$ possess semiconducting indirect band gaps of 1.64 eV and 2.44 eV, respectively. Furthermore, an investigation of the optical properties based on the complex dielectric function demonstrated that both compounds exhibit very high absorption coefficients in the order of $10^5\ cm^{-1}$ in the visible and UV regions. These results highlight the adaptability of these materials, indicating their potential for optoelectronic devices.

I. Ab-initio calculations method:

The Density Functional Theory (DFT) is a fundamental approach used in computational modeling to explore diverse characteristics of solid-state materials, including their structural, electronic, and optical properties. The FP-LAPW approach is crucial for DFT computations. The contemporary adaptation of the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional in the Generalized Gradient Approximation (GGA) optimizes ground state properties but underestimates some electronic characteristics. To address this limitation, our method employs the modified Becke-Johnson potential (TB-mBJ), significantly improving the accuracy of band gap predictions. The wave vector cutoff was set at $R_{mt} \times K_{max}$=7.5, the angular momentum vector l_{max}=10, and the most comprehensive Fourier expansion for charge density extends up to G_{max}=12 $a.u^{-1}$. When optimizing geometry, the convergence criteria for energy were set at $10^{-6}\ Ry$. To thoroughly cover the Brillouin zone (BZ), a dense k-mesh of 12×12×12 was used for electronic and structural properties. Additionally, to calculate optical properties, we increased the number of k-points to 36×36×36.

II. Results and discussion:

❑ Structural Properties:

Our study consisted in optimizing the structures of the double perovskites $Cs_2AgSb(Cl,Br)_6$ using the PBE exchange–correlation function. To obtain the equilibrium volume values by adjusting the energies as a function of volume. The cubic structure of the double perovskite with the space group Fm3m is illustrated in Fig. 1.
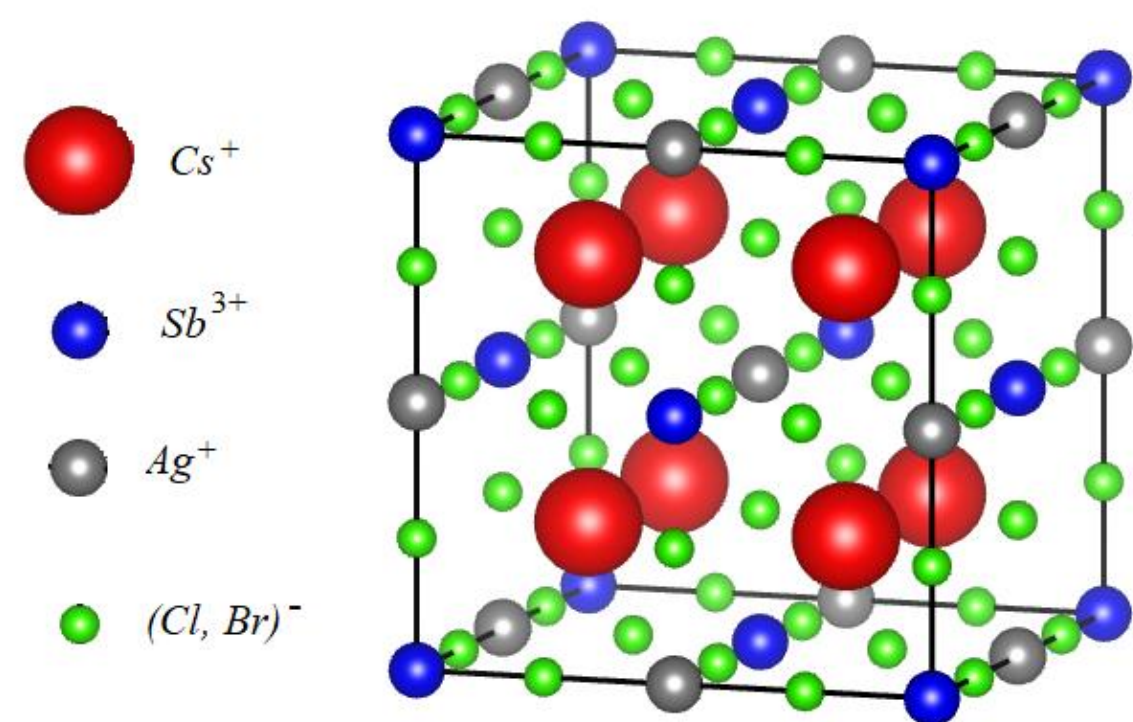

Fig. 1. The structure of double halide perovskite $Cs_2AgSb(Cl,Br)_6$.

Fig. 2 shows the variation of energy as a function of volume for $Cs_2AgSbCl_6$ and $Cs_2AgSbBr_6$, which correspond to optimized lattice constants of 10.86 Å and 11.36 Å, respectively. Our findings align closely with experimental materials [1,2].
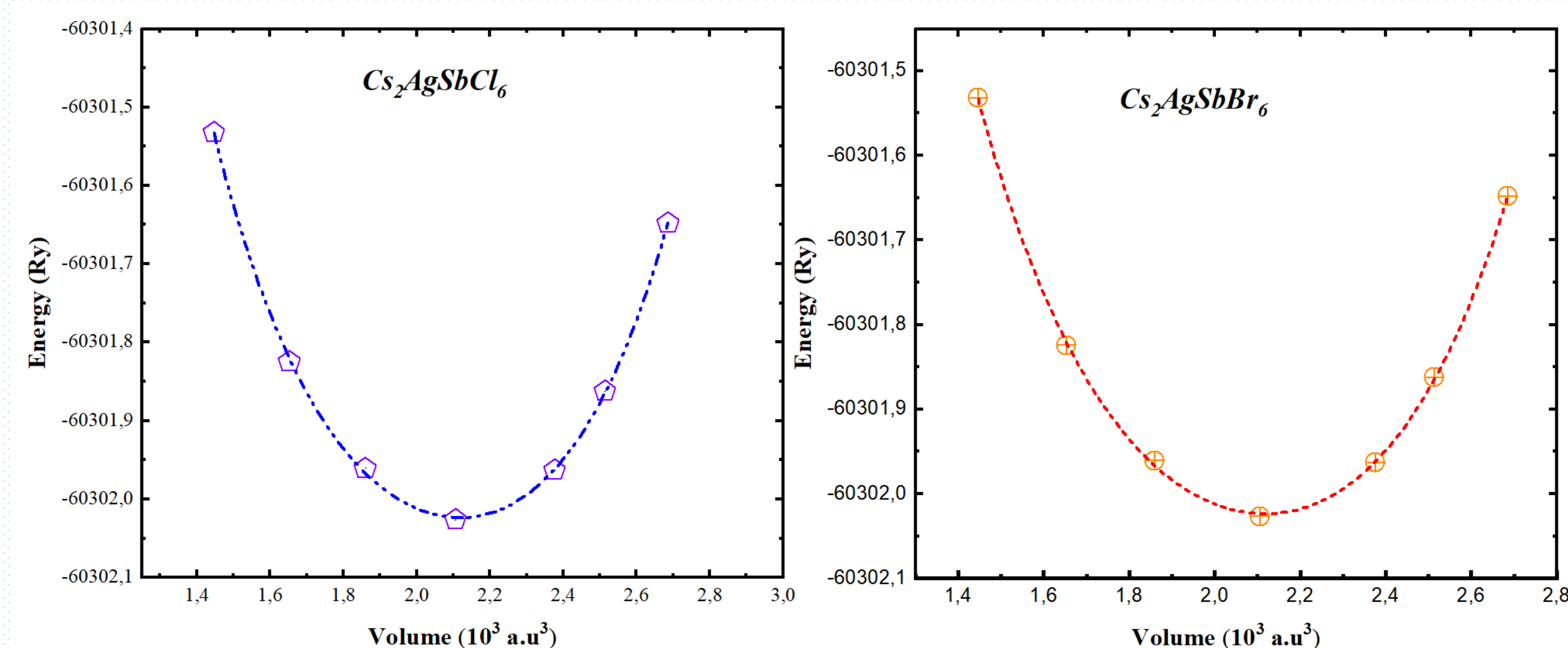

Fig. 2. The energy variation as a function of volume of $Cs_2AgSb(Cl,Br)_6$.

❑ Electronic properties and energy gap

The study of band structures offers valuable insights into energy levels and permissible electronic transitions. Fig. 3 vividly depicts the electronic band structure. The band structure diagram shows that both $Cs_2AgSbCl_6$ and $Cs_2AgSbBr_6$ display an indirect bandgap. In these compounds, the valence band (VB) maximum resides at a high symmetrical point (X), while the conduction band (CB) minimum is situated at a high symmetrical point (L) within the first Brillouin zone. The calculated bandgap values are 2.24 eV and 1.64 eV for $Cs_2AgSbCl_6$ and $Cs_2AgSbBr_6$, respectively, which align closely with the experimental values (E_g = 2.35 eV for $Cs_2AgSbCl_6$ and E_g= 1.64 eV for $Cs_2AgSbBr_6$) [3,4].

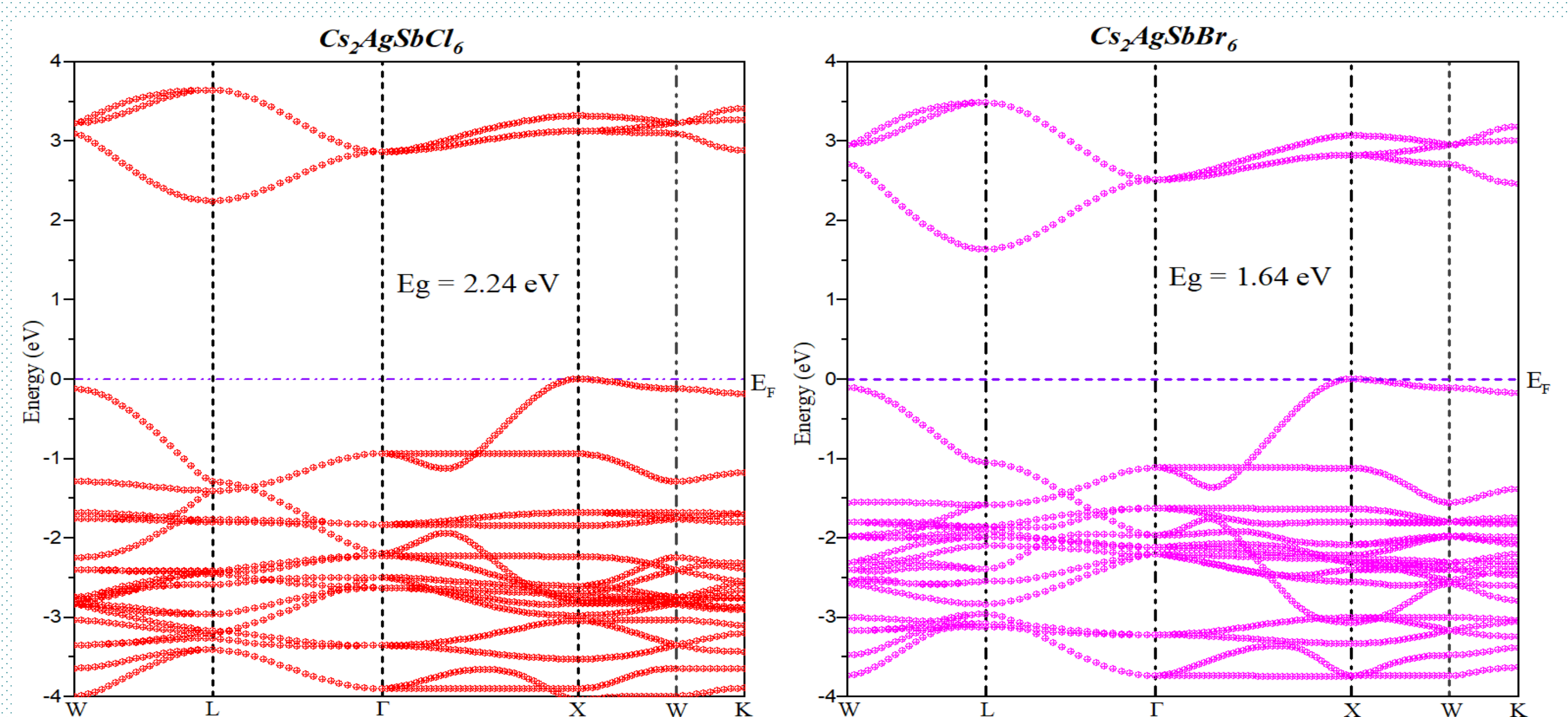**Fig. 3.** The band structures of $Cs_2AgSb(Cl,Br)_6$ from PBE+TB-mBJ

❑ Optical Properties:

In Fig. 4, we depict the absorption coefficients as a function of wavelength of $Cs_2AgSb(Cl,Br)_6$. Both compounds exhibit initial absorption peaks in the visible and ultraviolet spectra. Additionally, the highest absorption for both materials occurs within the ultraviolet range. Further-more, at 380 nm, $Cs_2AgSbBr_6$ absorbs at a rate of $2.38 \times 10^5\ cm^{-1}$, while $Cs_2AgSbCl_6$ absorbs at a rate of $2.74 \times 10^5\ cm^{-1}$, with absorption rates diminishing as the wavelength extends toward the infrared spectrum. When light interacts with the surface of a material, it undergoes simultaneous reflection, transmission, and absorption processes.
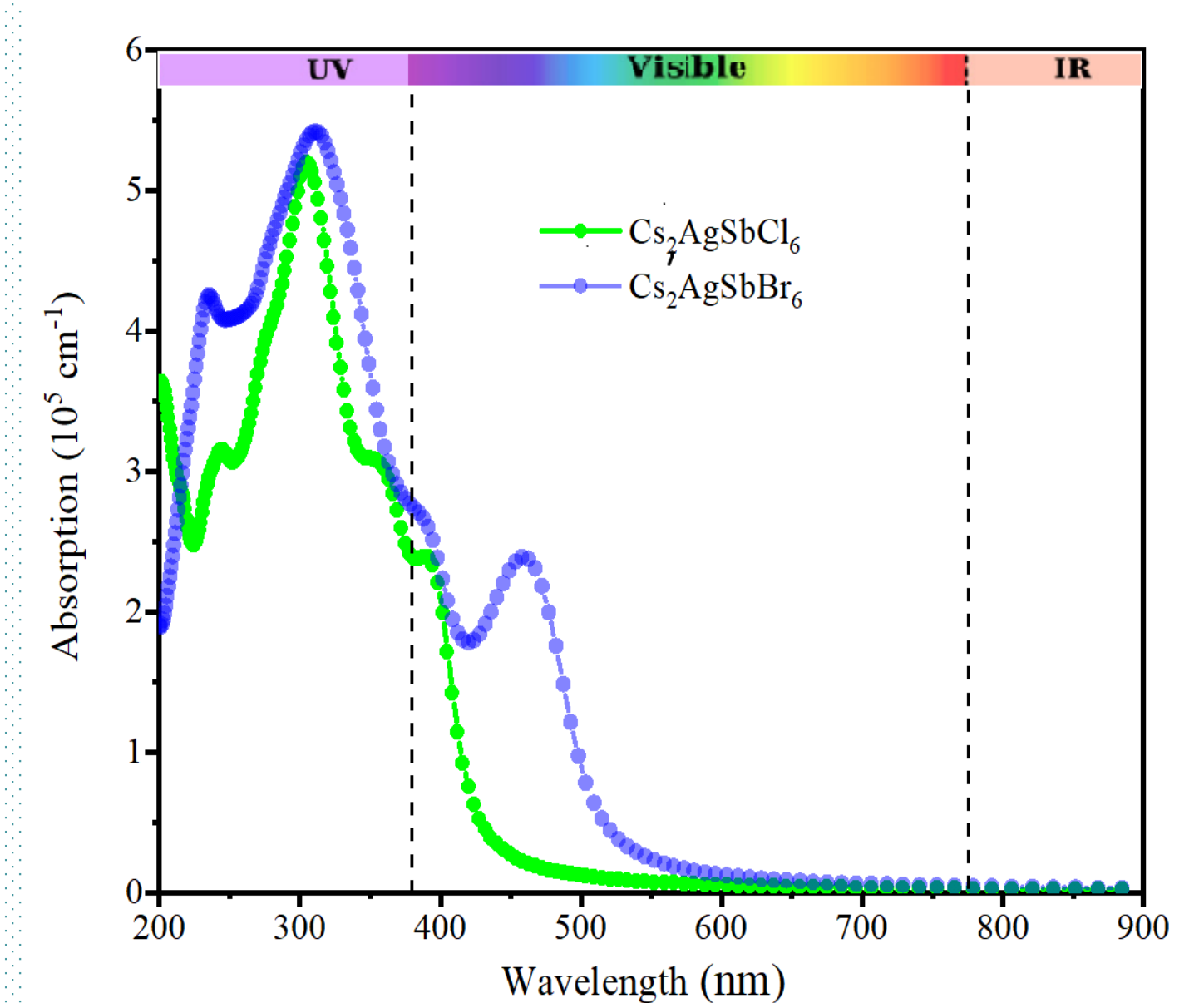

Fig. 4. The absorption spectra versus wavelength.

III. Conclusion:

In summary, we conducted an extensive investigation into the structural, electronic, and optical properties properties of $Cs_2AgSb(Cl,Br)_6$ using the density-functional theory framework. To achieve precise results, we used the TB-mBJ potential in conjunction with the FP-LAPW method, recognized for its predictive precision. The electronic band structure demonstrates semiconductor behavior, manifesting indirect bandgaps of 1.64 eV for $Cs_2AgSbBr_6$ and 2.44 eV for $Cs_2AgSbCl_6$. In addition, the absorption spectrum is predominantly situated in the visible region, with values approximately at $2.38 \times 10^5\ cm^{-1}$ for $Cs_2AgSbBr_6$ and $2.74 \times 10^5\ cm^{-1}$ for $Cs_2AgSbCl_6$. These findings suggest that the halide double perovskites $Cs_2AgSb(Cl,Br)_6$ exhibit significant potential for utilization in energy harvesting applications within practical devices.

Refernces:

[1] Wan Deng, et al., Appl. Phys. Lett. 111 (2017) 151602.
[2] Fengxia Wei, et al., Cheetham, Chem. Commun. 55 (2019) 3721–3724
[3] W. Smit, G. Dirksen, D. Stufkens, J. Phys. Chem. Solid 51 (1990) 189–196.
[4] G. Ding, G. Gao, K. Yao, Sci. Rep. 5 (2015) 9567.