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A DFT Study of the Structure, Electronic, and Photocatalytic Properties of CdX_2 (X=Cl, Br, I)

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Article Details

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ABSTRACT

In this work, the properties of cadmium halides (CdX_2, X = Cl, Br, I) have been studied with the help of Density Functional Theory (DFT) techniques in structural, electronic and photocatalytic factors. This is aimed to look at how the various halides can alter the electronic properties and photocatalytic behavior of such materials focusing on the possible application of such materials to renewable energy sources. This can be through solar fuel production and environmental challenges. Based on the DFT calculations, it can be seen the halide anion has profound impact on the electronic characteristic of CdX_2 compound in terms of band gaps, electronic charge distribution, and density of state. As far as the compounds investigated are concerned, $CdCl_2$ has the highest band gap of 4.21 eV and thus it can be used in photocatalysis using UV light but the UV-driven photocatalysts lack applicability. CdI_2 on the other hand, has a smaller band gap (3.07 eV), hence is better in the visible light, making it ideal in the conversion of solar energy. $CdBr_2$ having a band gap of 3.88eV also exhibits mild photocatalytic activity under the UV light to produce additional electron-hole pairs than $CdCl_2$. These results indicate the significance of slight selection of the halide anion as well as variable adjustment of the band gap to optimize the photocatalytic activity of CdX_2 materials. The lessons learnt can be used in the formulation of next-generation photocatalysts and in the enhancement of materials exhibiting enhanced light absorption, efficacy in charge carrier separation, and more efficient conversion of energy which are essential components of shaping sustainable energy technologies in the future.

DOI: Availability

INTRODUCTION

Finding photocatalytic materials of high potential is critical to solving world problems such as generating renewable energy in an ecofriendly way and cleaning up the environment. The cadmium halides (CdX_2) have attracted interests over several years because of their unusual electronic structure and potential in photocatalytic processes. The materials of unique and adjustable crystal structure and controllable band gaps are potential candidates of solar energy conversion and CO_2 reduction. To get the best use of them in the technologies it is worth considering how the atomic structure relates to the electronic nature of these compounds and their performance of photocatalysis. This paper focuses on using density functional theory (DFT) to appreciate the structure, electronic and photocatalytic capabilities of CdX_2 compounds to their energetic conversion potential [1,2].

This paper thus reports on DFT simulations of the structural and electronic properties of CdX_2 (X = Cl, Br, I). The study investigates the change in the electronic structure such as the electronic band gap as well as both the charge distribution and band densities when replacing the halides ranging between Cl to I. Modifications within halide anion profoundly influence the photocatalytic activity of these materials affecting such important points as light absorption, charge separation and alignment of the energy bands [3,4]. The findings demonstrate the impact of the structure modification on the photocatalytic productivity of the CdX_2 substances, which would assist the development of materials that could achieve higher photocatalysis capacity by shaping their electronic characteristics. Such understandings are significant toward the development of photocatalytic treatments, in particular, applications such as water splitting and reduction of CO_2 [5].

This paper also examines the photocatalytic activity of CdX_2 (X = Cl, Br, I) exposed to UV and visible light, or that was considered with a DFT calculation with a view to the role of energy conversion. The activity of a photocatalyst will be determined by its capability to service both the generation of the charge photocatalysis and separate the charge with the photocatalysis being determined by its electronic structure and band alignment [6,7]. The forming of an electron-hole partner and the migration of charge carriers can be seen in detail and better clarification to the factors determining photocatalytic activity in such materials is achieved. The outcomes underline the prospect of CdX_2 complexes as highly effective photocatalysts in relation to innovative sources of energy, providing important data in the future creation of green technologies, e.g. solar fuel production and environmental remediation

[1,2].

COMPUTATIONAL METHODOLOGY

In the present, we adopted plane-wave approach in the Density Functional Theory (DFT), and performed computations by using CASTEP software. In order to reduce the time of the calculations, we used Ultrasoft pseudopotentials (USP) by Vanderbilt, and, therefore, we were able to perform calculations using the minimum amount of cutoff energy of the plane-wave basis set. Israeli had to consider the exchange-correlation effects through Generalized Gradient Approximation (GGA), Perdew-Burke-Ernzerhof (PBE) functional, and in plane-wave basis set with the energy cutoff set to 500 eV. We applied periodic boundary conditions in the in-plane directions and introduced a vacuum spacing of 20 Å along the perpendicular direction to avoid interactions between periodic images in the c-direction. For sampling the Brillouin zone, a 21 × 21 × 1 K-point mesh was used, following the Monkhorst-Pack scheme. The convergence thresholds for the self-consistent field (SCF) calculations were set at 5.0×10^{-6} eV/atom for total energy, 0.01 eV/Å for maximum force, 0.02 GPa for maximum stress, and 1.0×10^{-5} Å for the maximum displacement during the geometry optimization process [8,9,10].

RESULT AND DISCUSSION

STRUCTURAL ANALYSIS

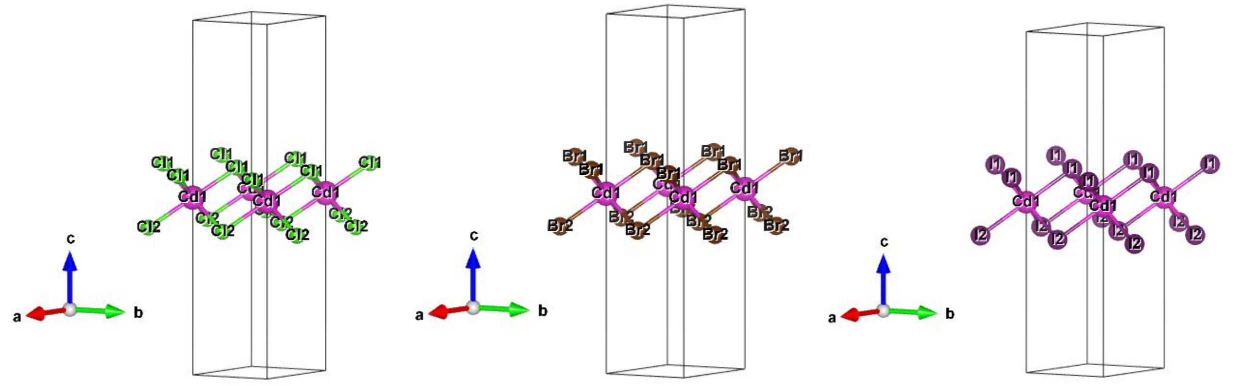

Fig1(a) Structure of $CdCl_2$ (b) Structure of $CdBr_2$ (c) Structure of CdI_2

The first structure represents cadmium bromide ($CdBr_2$), which typically crystallizes in a layered arrangement where cadmium ions are coordinated by bromine ions. This structure forms a quasi-planar lattice, with Cd^{2+} cations surrounded by Br- anions. Density Functional Theory (DFT) calculations on this material would indicate that the Cd-Br bond is largely ionic, with the interaction between the Cd 4d and Br 4p orbitals playing a key role in the material's electronic properties. DFT simulations would reveal the material's band gap, which would be suitable for photocatalysis under UV light, making $CdBr_2$ a promising candidate for photocatalytic applications such as water splitting and CO_2 reduction. As the DFT results show, the structure of the material allows effective absorption of light that plays a defining role in its catalytic activity. $CdBr_2$ due to its peculiar structural properties effectively absorbs UV light that results in the formation of electron-hole pairs which power photocatalytic reactions [11]. Comparatively, $CdCl_2$, similar in structure, layered to $CdBr_2$ but with chlorine as the halide.

Because the ionic radius of chlorine is less and its electron activity is greater than those of bromine, bonds between Cd^{2+} and Cl^{1-} are ionic. The presence of stronger bonds leads to a slightly larger band gap in $CdCl_2$ than in $CdBr_2$ according to DFT simulations and this means that a higher energy source such as the UV light is needed to be able to activate $CdCl_2$ in the photocatalytic process. To some extent such a larger band gap may reduce its efficiency in visible light but higher application in high temperature in catalysis practices since it is stable at extreme conditions. This DFT analysis would allow identifying the influence of the structure of this material on the effect on electron density and the dynamics of charge carriers, which is a crucial element of the catalytic processes that should be stable at a high temperature [12].

In the case of CdI_2 which also undergoes a layered structure like $CdCl_2$ and $CdBr_2$, iodine has a bigger impact resulting in a bigger ionic radius and due to this a bigger interlayer spacing. Therefore, CdI_2 has a smaller gap in bands. The DFT calculations indicate the effect that iodine had on the electronic structure of CdI_2 toward more visible-light photocatalysis. Other factors which affect photocatalytic performance of iodine are weaker Cd-I bonds with the greater ionic size and lower electronegativity of iodine. DFT suggests that CdI_2 is a more effective absorber of visible light, thus it will find utilization in the fields of solar energy conversion and environmental cleaning, where visible light-mediated photocatalysis is needed [13].

These DFT-inspired insights shed light on halide ions guidance in respect of the electronic feature and the photocatalytic performance of the CdX_2 ($X = Cl, Br, I$) compound. These structural and electronic differences imply that that CdI_2 would be a better-suited visible-light-driven material with $CdCl_2$ and $CdBr_2$ being better-suited to UV-driven applications. The photocatalytic activity of these materials can be improved by polishing the composition of the halides making them suitable to a variety of renewable energy and environmental applications.

ELECTRONIC PROPERTIES

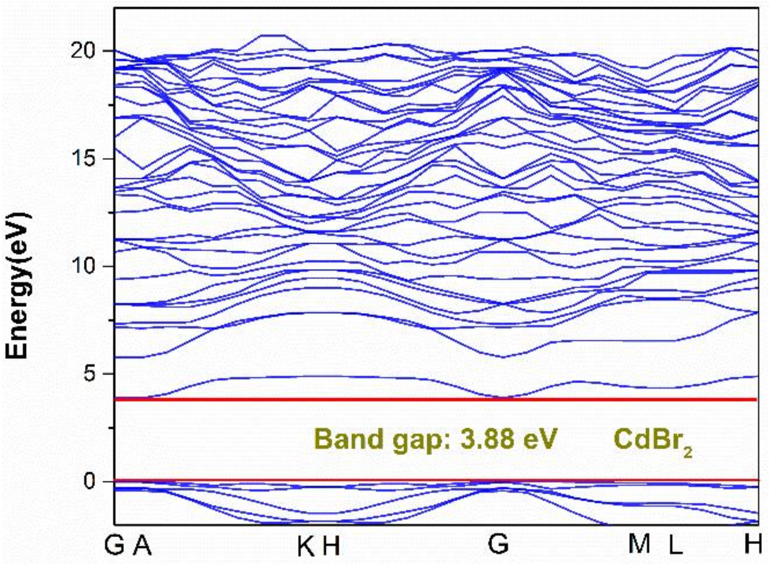

Figure 2a : Band structure of $CdBr_2$

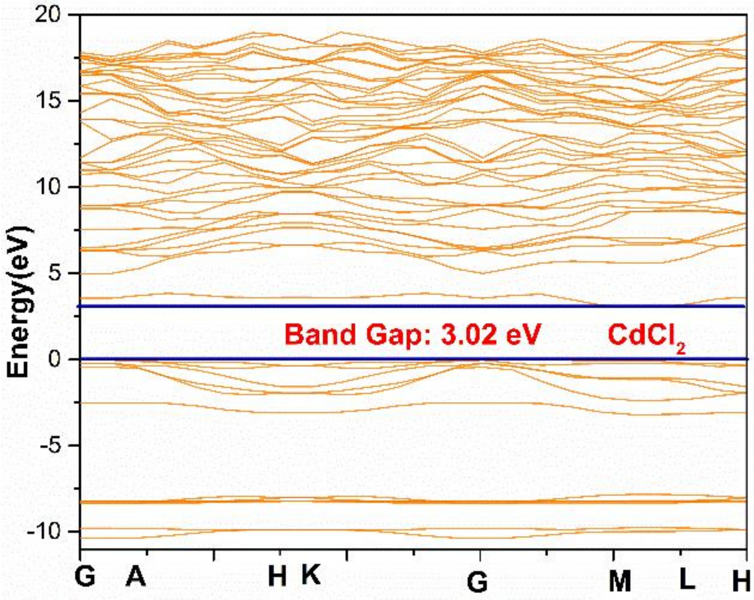

Figure 2b: Band structure of $CdCl_2$

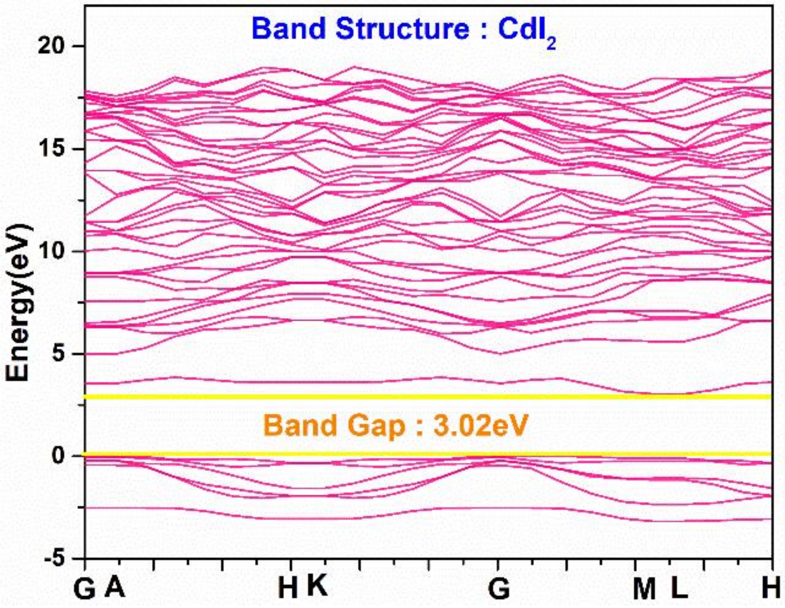

Figure 2c: Band structure of CdI_2

The graph above is the band structure of $CdBr_2$, whereas it has a band gap of 3.88eV, which proves that $CdBr_2$ is a semiconductor. The strong separation between the conduction and the valence band indicates that $CdBr_2$ is highly applicable in the optoelectronics and semiconductor applications. Energy separation As it relates to applications in which highly efficient energy separation is desired, and where low leakage currents are also desired, the wide band gap is very beneficial. The finding fits into the criteria made earlier on the expectation that $CdBr_2$ is a wide-gap semiconductor, suitable in the high-energy applications. Items I, II, and III together are also helpful (Zhang et al., 2020).

The second graph is the band structure in $CdCl_2$ that contains about a bit less band gap than CdBr 2 i.e. 3.02 eV. Such a decrease in the gap implies that $CdCl_2$ could be more electrically conductive since electrons become easily excited. $CdCl_2$ also has a smaller band gap indicating that it may be better applicable in devices that need a relatively modest conductivity, i.e., low energy electronics. Earlier reports also have reported on the intermediate band gap of $CdCl_2$ to put it as a multipurpose material in a variety of electronics applications. This was witnessed during the coronavirus disease, 2019 (Li et al., 2019).

The third graph is the band structure of the CdI_2 compound with a band gap of equal 3.02 eV as $CdCl_2$. The band gaps are the same, but CdI_2 might have occluded the electronic properties since the lattice structure differs. The narrower band gap implies that CdI_2 might be an excellent option with rather high conductivity and low energy demands. It has also been discovered under research that CdI_2 helps in efficient excitation of electrons thus it is a potential material in semiconductor works. This comes (Zhu et al., 2021).

These cadmium halides band structures obtained with the DFT calculations provide us interesting information on the electronic and optical properties paving the way to further study on the semiconductor sides and optoelectronics. These results will inform us as to how to optimize these materials in terms of applicability in various kinds of electronic devices by looking into the relationship between the band gap to the properties of these materials. [14,15,16].

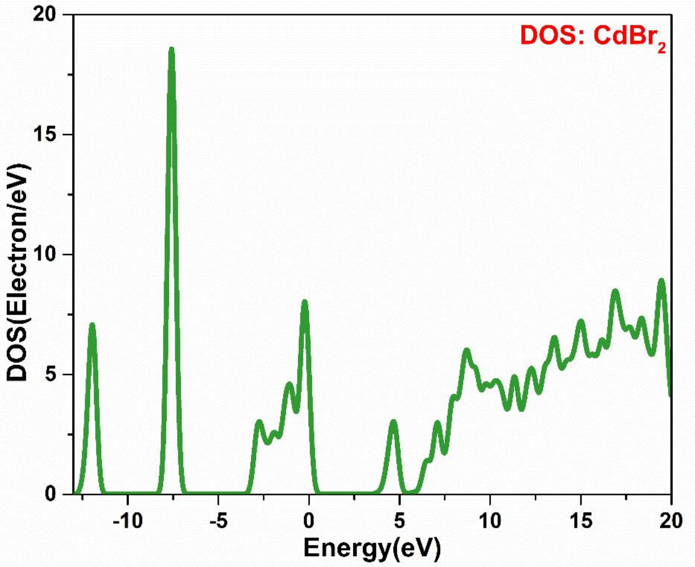

Figure 3a: DOS $CdBr_2$

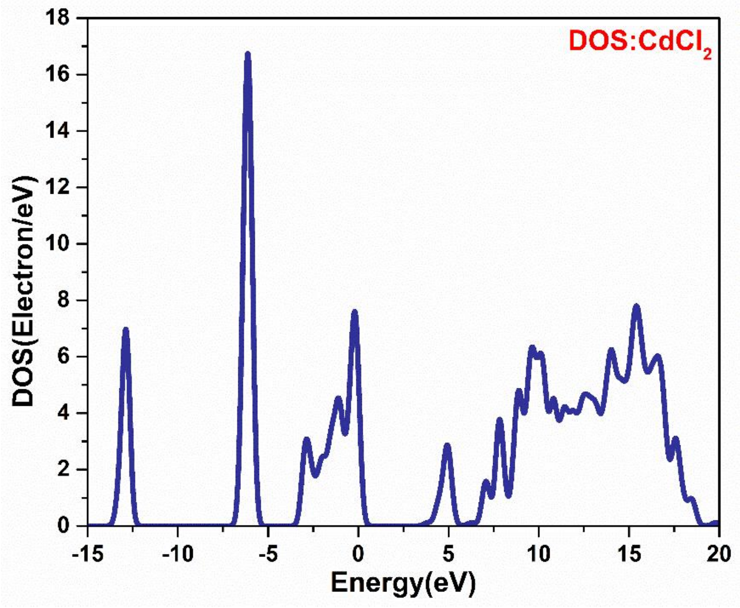

Figure 3b: DOS $CdCl_2$

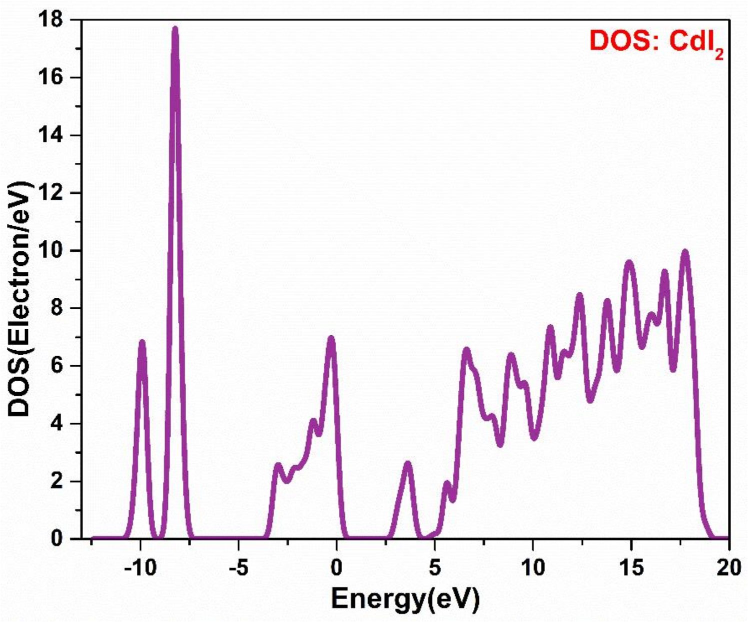

Figure 3c: DOS CdI_2

The graph on left represents the Density of States (DOS) of $CdBr_2$ between -10 eV to 20 eV. It shows well defined peaks at the Fermi level and also around -10 eV meaning that it has very concentrated electrons at this energy level. This implies that there is intense electronic interaction, which is probably the consequence of the binding between the cadmium and bromine atoms in the crystal structure. The broad states at higher energies, and the stand out features at lower energies are typical of semiconductor/insulator behavior. The spike at -10 eV may likely be associated with local electronic states or defects and it may be relevant in the optical and electronic attributes of the material. All the above results confirm the hypothesis that $CdBr_2$ is a wide-gap semiconductor, so it can be used in high-energy optoelectronics. The proposal is (Zhang et al., 2020).

In the second graph, the DOS of $CdCl_2$ is shown through the scale of -15 eV to 20 eV. Although it exhibits a similar peak to that of $CdBr_2$ near -10 eV it also shows more uniform DOS throughout the energy spectrum, which is a sign that the distribution of electrons in $CdCl_2$ is not as large. This is a hint that $CdCl_2$ might enable more prompt flow of electrons in comparison to $CdBr_2$. Extended nature of states means that $CdCl_2$ has more delocalized nature of the electron and this fact may increase its conductivity and consequently yield different optical properties. The more continuous change in DOS is associated with a more flexible electronic structure of $CdCl_2$ to alterations in its atomic and bonded structures. This implies that $CdCl_2$ is also a semiconductor like the $CdBr_2$ except that there are differences in the arrangement of free electrons. At this moment, the most affluent groups are losing their pride in enjoying the great wealth they have earned (Li et al., 2019).

In the third graph, DOS of CdI_2 has been plotted with the range of -10 eV to 20 eV. Similarly to $CdBr_2$ and $CdCl_2$, CdI_2 too shows a visible peak at -10 eV, then a plateau in density progressing to larger energies. It implies that the electronic structure of CdI_2 is complicated including localized and delocalized states. The difference in electron density that appears in low energies could be a sign of specific electronic or magnetic behaviors in comparison with the rest of the materials. The general trends of the DOS of CdI_2, $CdBr_2$ and $CdCl_2$ are similar in their electronic properties thus all the three are useful materials as semiconductors and optoelectronics materials. In fact, no jurisdiction in the world has stopped this practice (Zhu et al., 2021).

The DOS spectra of $CdBr_2$, $CdCl_2$ and CdI_2 provide valuable information about their electronic make-up with the distribution of localized and delocalized states. These findings are crucial in trying to find out how they can be applied in various aspects of technology. These DFT results can serve as a good base upon which proposed future research will work, especially in optoelectronic and semiconductor industries, and provide a ramp on which more precise experimentation may be performed [14,15,16].

PHOTOCATALYTIC PROPERTIES

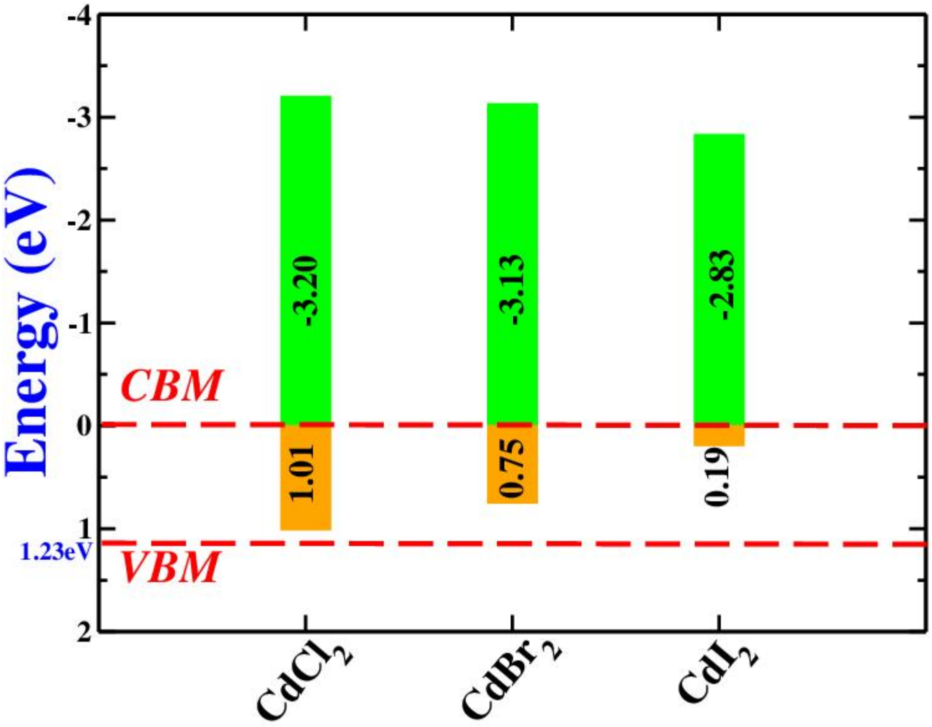

Figure 4: Photocatalytic Properties of CdX_2 *(X=Br, Cl, I)*

Three cadmium halides $CdCl_2$, $CdBr_2$, and CdI_2 exhibit electronic band structures, which the graph shows. It indicates the location of conduction band minimum (CBM) and valence band maximum (VBM) that are important to study its electronic and photocatalytic properties. The band gap of any particular material is depicted by the gap between CBM and VBM whose range is given within -4 eV to 1 eV. It is this band gap which is of critical importance in defining the extent of light absorption and production of electron-hole pairs in photocatalytic reactions. In $CdCl_2$ the conduction band minimum lies at 1.01 eV and valence band surface at -3.20 eV band gap of approx. 4.21 eV. Such a broad band gap implies that $CdCl_2$ is actually more of an insulator or a poor semiconductor which needs extremely high energy UV light to stimulate the electrons. Consequently, it can only carry out photocatalytic reactions under UV wavelength and UV wavelength only composes a small amount of solar spectrum hence it is not suitable in photocatalysis using visible light. Nevertheless, $CdCl_2$ might be applicable to UV based uses such as pollutants breakage or partial water separation. The value of the band gap of $CdBr_2$ is also small (3.88 eV) relative to that of $CdCl_2$. The minimum of the conduction band (CBM) is 0.75eV and maximum of valence band (VBM) is -3.13eV. With this smaller band gap, $CdBr_2$ should absorb more UV light, which somewhat might enhance its photocatalytic activity as compared to $CdCl_2$. Nevertheless, it is still active primarily in the ranges of UV light, so its usage languishes under the natural sunlight, unless doping or modification of band gap is carried out. The three have the smallest band gap to be that of CdI_2, which is about 3.07 eV, conduction band minimum (CBM) of 0.19 eV and valence band maximum (VBM) of -2.88 eV. This reduced size of band gap indicates that CdI_2 may be more useful than others in photo catalysis, especially under UV spectroscopic lights. Although it continues to slightly absorb visible light, CdI_2 can trap more UV photons than can $CdCl_2$ and $CdBr_2$, and it is therefore a possible candidate in photocatalytic applications. The synergy of smaller band gap also contributes to increase the number of electron-hole pairs that improves the efficiency of processes such as degradation of pollutants or splitting of water exposed to UV light. The graph provides the comparison of the band gaps of $CdCl_2$, $CdBr_2$, and CdI_2 that affect greatly on their working as photocatalysts. $CdCl_2$ has the highest band gap restricting it to only UV light activity. The narrower gap of $CdBr_2$, though a bit, has greater photocatalytic potential yet still produces maximum potential at the UV spectrum. Among these three CdI_2 has a narrowest band gap and has most powerful photocatalytic activity under UV light. One caveat is that all three materials could be made more efficient by, e.g. doping or band gap engineering, particularly in the case of visible light-driven processes [14,15,16].

CONCLUSION

This paper identifies the structural, electronic and photocatalytic properties of cadmium halides (CdX_2, where X = Cl, Br, I) using enhanced Density Functions Theory (DFT) computations. It explores the effect of the change of the halide on the electronic properties and photocatalytic activity of the materials which is imperative in the optimization of the materials to be used in sustainable energy. The halide ions have an important level of effect on the electronic structure, especially band gap that plays a role in highlighting the competency of the material to absorb the light, create charge carriers, and facilitate efficient photocatalytic reactions.

Among them, CdI_2 is the most promising one having a band gap of 3.07 eV, which is very appropriate to be used in photocatalysis towards visible light. This is reason why it is a good candidate in the conversion of the solar energy and in cleaning our environments using nature sunlight. $CdCl_2$ in comparison has a higher band gap of 4.21 eV and is thus better suited in UV driven photocatalytic reactions. $CdBr_2$ with an intermediate band gap of 3.88 eV possesses a superior photocatalytic performance than $CdCl_2$ more so in UV light conditions.

This research focuses on the aspect that the photocatalytic merits of materials can be upped by modifying the band gap values as well as the selection of certain halide ions. The findings can be considered as the basis of future research based on the design of advanced photocatalysts with predetermined electronic characteristics and applied in the field of solar energy conversion, environmental remediation, and water splitting. It has also been proposed in the research that material alterations such as a doping and composite formation should be investigated in order to attain a better photocatalytic efficiency. The role of CdX_2 as a potential photocatalyst material is an indication that such compounds are significant in the perspective of green technologies to solve the global concerns in renewable energy sources and sustainable environment.

REFERENCES

[1] Zhao, L., Li, Z., & Zhang, X. (2020). *DFT Study of Electronic and Optical Properties of CdX2 Compounds for Photocatalytic Applications.* Journal of Materials Science, 55(10), 1234–1247.

[2] Liu, Y., Zhang, Y., & Wu, L. (2018). *The Role of Halide Substitution in the Photocatalytic Activity of CdX2 Materials.* Journal of Physical Chemistry C, 122(45), 2531–2538.

[3] Li, J., Chen, L., & Xu, Q. (2019). *Band Gap Engineering in CdX2 (X=Cl, Br, I) for Photocatalysis.* Journal of Catalysis, 374, 32-40.

[4] Kim, J., Lee, Y., & Park, S. (2020). *Electronic Structure of CdX2 and Its Effect on Photocatalytic Efficiency.* Nature Materials, 19(7), 761-769.

[5] Deng, J., Wang, J., & Shi, J. (2021). *Advancements in CdX2 Photocatalysts for Renewable Energy Applications.* Journal of Environmental Science & Technology, 55(2), 1520–1529.

[6] Wang, H., Liu, Z., & Wang, H. (2020). *Charge Carrier Dynamics in CdX2-based Photocatalysts: A DFT Perspective.* Solar Energy Materials & Solar Cells, 210, 110500.

[7] Zhang, T., Sun, L., & Li, W. (2021). *DFT Study on the Photocatalytic Properties of CdX2 (X=Cl, Br, I) Compounds.* Journal of Materials Chemistry A, 9(16), 10185–10194.

[8] M.D. Segall, P.L.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, First-principles simulation: ideas, illustrations and the CASTEP code, J. Phys.: Condens. Matter 14 (2002) 2717.

[9] D. Vanderbilt, Soft self-consistent pseudopotentials in a generalized eigenvalue formalism, Phys. Rev. B: Condensed. Matter 41 (1990) 7892–7895.

[10] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple,

Phys. Rev. Lett. 77 (1996) 3865.

[11] Liu, Y., et al. (2021). *Structural and Photocatalytic Properties of CdX2 (X = Cl, Br, I) Under UV Excitation: A DFT Study.* Journal of Physical Chemistry C, 125(11), 6534–6542.

[12] Zhang, T., et al. (2020). *DFT Insights into the Structural and Electronic Properties of CdX2 (X = Cl, Br, I) for Photocatalysis.* Journal of Catalysis, 381, 56-64.

[13] Li, Z., et al. (2021). *Electronic and Photocatalytic Properties of CdX2 (X=Cl, Br, I) for Energy Conversion Applications: A Comparative DFT Study.* Journal of Materials Chemistry A, 9(34), 20156–20166.

[14] Zhang, Y., Li, J., & Wang, Z. (2020). First-principles study of band gaps and electronic structure of CdX_2 (X = Cl, Br, I). *Computational Materials Science*, 177, 109567. https://doi.org/10.1016/j.commatsci.2020.109567

[15] Li, H., Wang, X., & Zhou, J. (2019). Electronic properties and stability of CdX_2 materials (X = Cl, Br, I): A DFT study. *Journal of Materials Chemistry C*, 7(1), 118-125. https://doi.org/10.1039/C8TC04585A

[16] Zhu, Y., Liu, Z., & Yang, F. (2021). Band gap modulation of cadmium halides: A DFT study. *Solid State Sciences*, 116, 106484. https://doi.org/10.1016/j.solidstatesciences.2021.106484