Structural, Electronic and Optical Properties of MgH2, CaH2 for Hydrogen Storage Materials: First principles study

Muhammad Irfan and Sikander Azam

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Muhammad Irfan[1], Sikander Azam[2],

[1]Department of Physics, The University of Lahore, Sargodha Campus, 40100 Punjab, Pakistan
[2]*Faculty of Engineering and Applied Sciences, Department of Physics, RIPHAH International University I-14 Campus Islamabad, Pakistan*

ABSTRACT

In this paper the electronic and optical properties of the effective hydrogen storage materials MgH_2 and CaH_2 are studied in detail using the most efficient GGA under the frame work of gradient corrected density functional theory. The calculated band structure and density of states analysis show that the material MgH_2 has insulating nature while CaH_2 exhibits semiconducting behaviour. The band gap values are discussed and compared with the other theoretical and experimental values. The optical behaviors of these two materials are analyzed by using the complex dielectric function, which is calculated and corrected by the scissor operation and these analysis are discussed based on the electronic structure of the two materials. In addition to real and imaginary parts of the complex dielectric function, absorption and extinction coefficient, refractive index, reflectivity spectra, real part of optical conductivity and the energy loss function which is a function of photon energy were calculated and discussed in details. The previous results obtained from literature and our calculated results were in a good agreement.

Keywords: DFT, Optical Properties, FPLAPW, Wien 2k

Corresponding Author: Muhammad Irfan (bilalirfan104@gmail.com)

1. Introduction

Metal Hydrides are the most fascinating materials having hydrogen (H) atoms bounded purely in ionic (H^- or H^+ ions), covalent, or in metallic (interstitial) forms with other elements [1]. These materials have expanded significant concentration because of their reversible hydrogen sorption behavior, which is out mostly responsible to fuel the world with its efforts to enhance and develop secure and useful hydrogen storage mediums for transportable applications [2-3]. These hydride metals are also mostly attractive because of their atomic or electronic structures and as of their many distinguished properties which includes (optical, electrical, thermal, etc.). They can be controlled in equivalently with the help of metal↔hydride transformation i.e. by variation of hydrogen pressure and necessary temperature conditions. These extraordinary characteristic have been implemented in numerous applications like smart sensors, windows, heat storage systems, cryogenic coolers and hydrogen compressors without using moving parts [4-7].

In electrochemical energy storage industry some of their other fascinating applications include the use complex boro hydrides which are solid electrolyte and the magnesium based hydride cathodes conversions mainly used in lithium-ion batteries [8-9]. These hydrides such as (BeH_2, MgH_2, CaH_2, SrH_2 etc) are extensively analyzed, in order to improve the knowledge about their optoelectronic proprieties which are used in a wide range of technological applications [10]. Among the two materials MgH_2 is a member of these alkaline earth hydrides which is formed as a result of reversible reaction of magnesium with hydrogen and is most extensively investigated both experimentally and theoretically due to its greater gravimetric which is about (7.6 wt %) and volumetric (108.7 g/ L) for hydrogen storage capacities. The slow reaction kinetics of hydrogen charge/discharge and its high temperature desorption are considered to be the two greatest shortcoming which intensively restricts the useful and practical applications of these magnesium based hydrogen storage materials [11]. There are recently some theoretical investigation carried which demonstrate that MgH_2 exhibits a wide variety in phase transitions which are function of pressure and high thermodynamic of MgH_2 and can aspect the relatively of stronger Mg-H bonding, forming a stable 4-fold-coordinated structure for the hydrogen atom in MgH_2 [12-13]. In addition some band structure predictions illustrate that MgH_2 has principally ionic nature with also a little covalence nature [14]. Some of the band gaps values which are in-between 3.1 eV and 4.2 eV for MgH_2 which were theoretical calculated by [using local-density approximation (LDA) and the generalized gradient approximation (GGA)] [15-17] are smaller than some of the reported sporadic experimental values so far. The Penn's formula was used as in direct way by Krasko and Pong and they determined an average band gap of 5.16 eV, 5.8 eV respectively for MgH_2 [18-19]. An observed shift of band gap for some higher energy was illustrated which was mainly due to formation of MgH_2 [20]. Similarly for the material CaH_2, which is known to be one of the two most valuable light metal hydrides (MgH_2 and CaH_2), an ionic bonding nature was observed by taking into consideration the separated electro-negativities of both Ca and H, which was confirmed by the Xps study [21]. The cubic CaH_2 formation with no fluoride content was inspected by the relative stability of both the orthorhombic and the cubic CaH_2 phases. These calculations were carried out both for the neutral vacancy and also for single negative charge vacancy. The structures which have no vacancies, from the cubic CaH_2 the orthorhombic CaH_2 phase was found to be more stable one. On the other hand, when hydrogen vacancies were introduced, it was found that cubic CaH_2 showed more stability than orthorhombic phase [22]. The generalized gradient approximation (GGA) first are used to insight the electronic and elastic properties of tetragonal MgH_2, orthorhombic CaH_2, and hexagonal $Ca_4Mg_3H_{14}$ phases. The interpreted band gap values for MgH_2, CaH_2 and $Ca_4Mg_3H_{14}$ were 4.22 eV, 2.99 eV, and 3.20 eV respectively, indicated that all these three hydrides were insulators. Similarly the calculated elastic constants of MgH_2 and CaH_2 showed mechanical stability at zero pressure for these two materials. The value of B/G ratio was lesser than 1.75 for these materials which clarify their brittle nature [11]. All these alkaline-earth metals demonstrate a switchable performance with a characteristic color in the completely hydrogenated state due to having their band gap in the visible region of the corresponding optical spectrum i.e. (E_g=3.02 eV) and also shown that alloying with Mg results in a color neutral switchable mirrors which are of utmost importance for various applications e.g. ‘‘smart’’ windows [23].An optical transmission spectrum of MgH_2 in case of a thin film was reported in which the observed transmission spectrum disappeared at 6.015 eV (206.1 nm) [24]. Similarly there was an index of refraction of about 1.95 and 1.96 for the ordinary and an extraordinary ray was at 588.3 nm [25]. This incited our interest to study the electronic and optical properties of MgH_2 and CaH_2 in detail by using GGA.

2. Computational details

We carried ab-initio calculations of these light metal hydrides i.e. MgH_2 and CaH_2 as an efficient hydrogen storage material by using the full potential linearized augmented plane wave (FPLAPW) method within the frame work of the state of the art density functional theory (DFT) and as implemented in the WIEN2K code [26-32]. The space is splited into an interstitial region and some non-overlapping spheres which are centered at atomic sites. In these calculations we took $R_{MT}K_{max}$ = 7.0 this determines the matrix size convergence, in above the plane wave cut off is Kmax and the smallest atomic radii is R_{MT}. When the energy of the two systems was stabilized at 10^4 Ry, the self-consistent calculations are considered congregated.

The complex dielectric function is used to get optical properties and is given by $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$

The real part $\varepsilon_1(\omega)$ of this dielectric function relates to the electronic polarizibility of material and the imaginary part $\varepsilon_2(\omega)$ describes electronic absorption of materials [33-34]. The imaginary part $\varepsilon_2(\omega)$ is given as

$$\varepsilon_2(\omega) = \frac{2\pi e^2}{\Omega\varepsilon_o}\sum_{c,v}\sum_{k}|\langle\psi_k^c|\hat{u}r|\psi_k^v\rangle|^2\,\delta(E_k^c - E_k^v - h\omega)$$

Where the term “Ω” in above gives the volume of the elementary cell, (*v*, *c)* shows the valence (VB) and conduction band (CB) respectively, term “ω” is frequency of incident light, and “*k”* represents the vector which define the polarization directions of the electric field having fully isotropic average value in a polycrystalline material [35]. The real part $\varepsilon_1(\omega)$ and the imaginary part $\varepsilon_2(\omega)$ are then further used to get other optical parameters which includes reflectivity *R(ω),* absorption coefficient *I(ω)*, refractive index *n(ω),* energy loss spectrum

L(ω), extinction coefficient *k(ω)* and optical conductivity. Our calculated unit cell structure for both the materials is shown in Fig. 1.

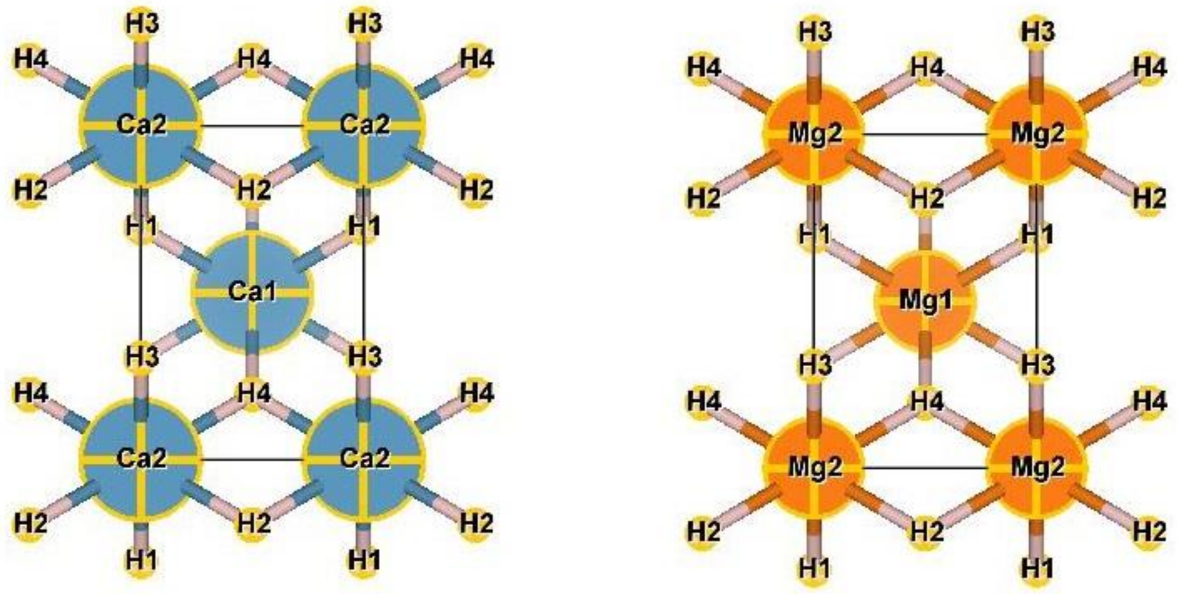


Fig.1: Calculated unit cell structure for MgH_2 and CaH_2.

3. RESULTS AND DISCUSSION

3.1 Electronic band structure and Density of states

One of the greatest ways to comprehend absolutely the electronic properties of metal hydrides is provided by band-structure investigations. The ground-breaking work along this path was first carried out by Switendick [36] in 1970 he used an augmented plane-wave (APW) method, that was able to explain the limits of the cut down images in the Ipc models after that a few number of other related band structure methods of calculations have been reported [37-38]. However, for CaH_2 material in its actual structure and having its low orthorhombic symmetry, there is band-structure calculation neither presented nor some other first-principles studies illustrated till. Weaver et al. performed only a single and a non self consistent APW band structure calculation for CaH_2 [39], in which CaH_2 material having complicated structure was simplified to some hypothetical CaF_2 type FCC structure. The band structure for both MgH_2 and CaH_2 calculated by using GGA are shown in Fig. 2 respectively and along with the corresponding band gap values which are listed in Table 1. As from the fig. 2 it is clear that in case of MgH_2, at the H site the charges are totally accumulated and are mostly depleted at the Mg site which is an indication of charge transfer from Mg site to corresponding H site and suggesting the presence of ionic bonding. We also know that the band gap values which are calculated with the help of GGA Eigen values in the DFT mostly underestimate the actual band gap value which basically due to the discontinuity of exchange-correlation potentials. We can modify the difference between actual excitation energies and the Kohn–Sham eigen value with a rigid shift of conduction band in term of valence band. As our calculated band gap by mean of GGA which is 4.91 eV for MgH_2 is in quite close agreement with that of the experimental band gap values which was reported to be (5.60 eV[40] and 5.16 eV [41]). Similarly in addition to this, our calculated results clarify the insulating nature of MgH_2. From these band structure calculation it also clear that the valence band gap maxima is in-between the 0 and X points and the conduction band minima is located on the R point in BZ which clarifies the indirect band nature for MgH_2 and by application of any elemental substitution in MgH_2 would reduce this band gap value. This high band gap value of MgH_2 recommends that it would be most valuable to yield solar energy in the ultra violet range. Similarly from GGA studies a band gap value of 2.01 eV was calculated for CaH_2 and the band structure (Fig.2) for CaH_2 suggests that it is a direct band gap material. In order to get a superior understanding related to the bonding character of these metallic hydrides, the electronic structure of these two materials was calculated which revealed the enhanced mechanism about their structural stability and corresponding optical features. The angular momentum projected (DOS) and (PDOS) were calculated for the two materials and is displayed in Fig. 3 which clearly shows that for MgH_2 in the valence band, the Mg-*p* state dominate the lowest region ranging from (-2.1 eV to -6.2 eV), where as the upper region which is from (0 eV to -2.1 eV) was dominated by the Mg-*s* state. Similarly in the region of conduction band (CB) ranging from (0 eV to 4.0 eV), Mg-*s* state proves to be more dominant than the corresponding Mg-*p* and H-*s* states. Fig. 3 also demonstrates that the effective role of Mg-*p* state is in greater concentration than that of H-*s* state in the given valence band (VB) and every individual Mg atom donates approximately 1.59 electrons to the corresponding neighboring H atoms, this character also indicates the presence of ionic bonding in case of MgH_2. Besides this, the H-*s* states are to some extent then hybridized with Mg-*p* and Mg-*s* state in the CB which is an indication of the presence of covalent bonding also. Our calculated density of states (DOS) results by GGA studies for MgH_2 illustrated in Fig. 3 also clarify that MgH_2 is an indirect band gap insulator type material. The (PDOS) illustrated in Fig. 3 for CaH_2 also shows that the Ca-s state dominate the both the lower grade regions and the upper grade regions in the valence band i.e. from (-6.8 eV to 0. eV), while as far as in case of conduction band the H-*s* states are to some extent hybridized with Ca-*p* and Ca-*s* states in the CB which points toward the presence of covalent bonding nature.

Table.1: Calculated band gap value by GGA+U for both the materials.

Light metal hydrides	Our work by GGA+U	Experimental work	Other theoretical work
MgH_2	4.91	5.60[40] 5.16[41]	3.60[14] 3.06[40] 4.29[44]
CaH_2	2.01	-----	3.16[45] 2.82[45]

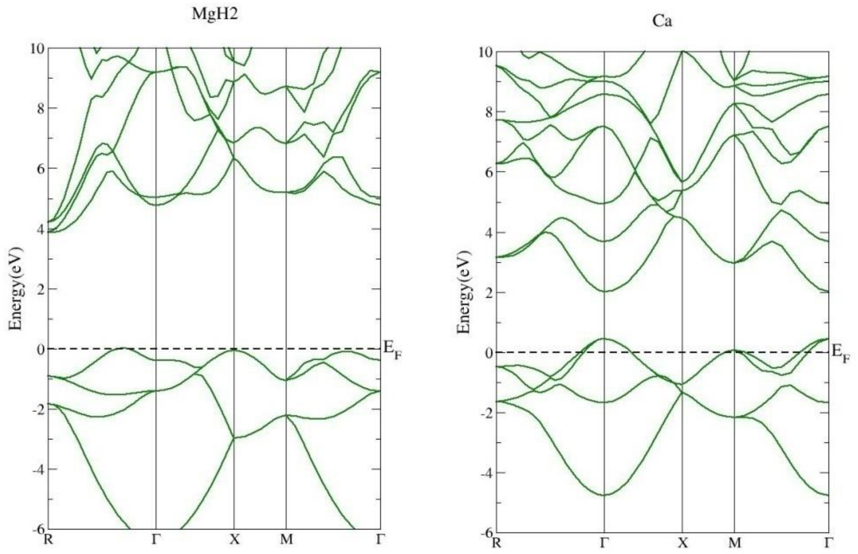


Fig. 2: Calculated Band Structure of the MgH_2 and CaH_2 respectively, plotted in the first BZ and the zero line correspond to EF.

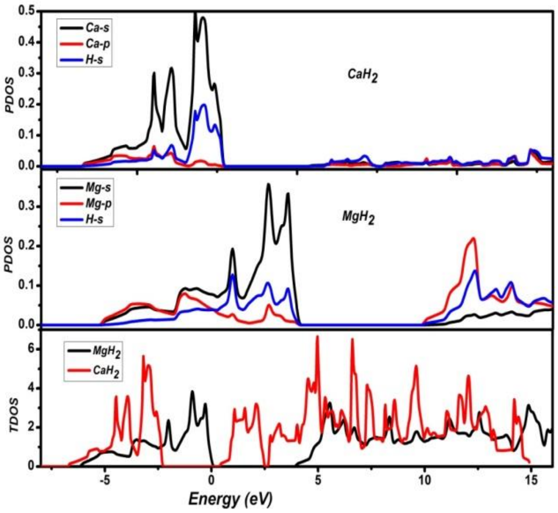


Fig. 3 : Calculated total (TDOS) and partial (PDOS) of the MgH_2 and CaH_2 and the energy is set at zero of EF

3.2 Optical properties

The optical properties of materials offers a very significant approach for the extensive study of energy band structure, impurity levels, lattice vibrations, magnetic excitations and different localized defects. In order to get the effective information related to the linear optical properties, the complex dielectric function i.e. $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is investigated which express full information about the polarization response of a certain system to an external electromagnetic field with the presence of a small wave vector. Various transitions in-between the occupied and unoccupied wave vector states are provided by the electric field of photon. The superposition of diverse mechanisms is totally involved in frequency dependence of the system. For a system in most cases, the all four essential mechanisms which are purely produce includes ionic polarization, interfacial polarization, orientation polarization of permanents dipoles and the electronic polarization. As our studied compounds which are purely in crystalline solid form and have partially ionic nature, so main contributions related to dielectric functions are mainly due to the two polarizations i.e. ionic polarization and electronic polarization and the other two (interfacial, Orientational) are most likely neglected. In addition for the imaginary part of dielectric functions $\varepsilon_2(\omega)$, the ionic polarization of the real function $\varepsilon_1(\omega)$ was neglected and then calculated by the help of Kramers–Kronig transformation [42]. Among these two metals hydrides, MgH_2 is being most intensely investigated to exploit its potential usage as H_2 energy carrier and also expanded its importance its applications in optical switching. Recently, some experimental results related to optical properties and the optical band gap energy is described by Paik et al [43] by using the electron energy loss spectroscopy which was in the Plasmon energy range in order to know about the optical band gap and determining its dielectric function. We therefore evaluated the optical properties such as dielectric function, refractive index, extinction coefficient, optical conductivity, absorption and reflection coefficient of MgH_2 and CaH_2 by using GGA with in the DFT approach. In order to look deeply into the optical properties and other related optical parameters we evaluated the complex dielectric function. The real part $\varepsilon_1(\omega)$ of the dielectric constant which is shown in fig. 4(a) is in the small energy range first start increasing with increase in the photon energy and then attains a maximum value of about 6.4 eV for CaH_2 and 9.8 eV for MgH_2, with the increase in photon energy it then start decreasing and reaches to a minimum value of about 1.32 at photon energy value of 4.1 eV for CaH_2. Similarly in case of MgH_2 it decreases to its minimum value of about 1.5 to the corresponding photon energy of 5.9 eV, the value of the dielectric constant increases once again but at an average value of 0.9 eV upto 9.8 eV become stable in case of MgH_2. The our illustrated static dielectric constant value calculated as $\varepsilon_1(0)$ = 3.29 for both the two materials are in an excellent agreement to the recent experimental values [31]. The reported energy for $\varepsilon_1(w)$ when it pass through zero along positive point is 10.31 eV, this value is also in fine agreement with the corresponding measured value i.e. 10.34 eV [43]. The reported three major peaks situated at 5.1 eV, 6.13 ev and 6.8 eV as shown in fig. 4(b) in the imaginary part of dielectric functions in case of MgH_2 show the electronic excitations. In these peaks the first peak is ascribed mainly because of transition from Mg-*p* states to Mg-*s* unoccupied states, where the second peak relates to inter band transition which is from Mg-*s* to Mg-*p* states and this shows the highest transition and the last peak is mainly due to the H-*s* electronic excitations. We compared theses transition energies i.e. (5.1 ev, 6.13 eV and 6.8 eV) in case of MgH_2 with the experimental band gap values of 5.16 eV [41] or 5.60 eV [40], in addition to this peaks at 2.9 eV, 7.2 eV, 8.7 eV and 9.45 eV are observed in imaginary part of CaH_2 which also specify the electronic excitation among Ca-s, Ca-p and H-s states. So the conclusion arises that optical assessment exceeds the band gap energy which is not considered to be a proper criterion for these band gap calculations. Similarly a larger anisotropy which is in the real part $\varepsilon_1(\omega)$ and in the imaginary part $\varepsilon_2(\omega)$ of dielectric function for these two compounds closer to the main peak is observed. To get value of the refractive index i.e. $n(\omega)$ for CaH_2 and MgH_2, a mathematical relation is employed, which is between the complex refractive index and the dielectric function, and given in [20], by using this relation the corresponding results are obtained which are displayed in figure 5(a). The refractive index n(0) = 1.865 eV for MgH_2 and n(0) = 1.921 eV for CaH_2 is in a fine agreement with that of experimental value which was 1.95 eV, measured by Ellinger et al [25] for MgH_2 and to the data of ellipsometry and spectrophotometry experiments which was 1.94 [20]. The absorption coefficient $I(\omega)$

indicating the portion of energy which is lost by the wave when passed through the material, is demonstrated in figure 5(b) for both these materials. Our illustrated results declares that there is neglected amount of absorption of energy for the range of photon energy less than 2.45 eV for CaH_2 and 4.41 eV for MgH_2. In case of CaH_2 the value of the absorption coefficient first start increasing at the photon energy greater than 2.45 eV, and approaches to a maximum value at 4.15 eV, similarly in case of MgH_2 it start increasing at 4.41 eV and then reaches to a maximum value at 5.6 eV. This elucidates and proves MgH_2 as a prospective material for the opto-electronics in ultraviolet region mainly due to its extremely sharp cut-off response particularly in this region. The shown in Fig. 5(c) gives the calculated real part of the optical conductivity which clarify and show that the optical conductivity vanishes in the energy range less than 2.8 eV and 3.6 eV for CaH_2 and MgH_2 respectively, on the other hand it becomes maximum at 5.3 eV and 6.9 ev for CaH_2 and MgH_2 respectively. These calculated results are analogous to the calculated band structures and the DOS results for the two materials. To get a further comprehensive knowledge related to the optical properties of these materials, we consider the electron energy-loss factor which gives information about the energy loss of a high-speed electron passing through a material. The energy lost by the high-speed electron is expressed by the energy loss function $L(\omega)$ and mathematically written as $1/\varepsilon(\omega)$. The structures of the $L(\omega)$ spectrum are mainly related to the plasma frequency which indicates the combined performance of the loosely bounded electrons in the valence and conduction bands. The electron energy loss function for CaH_2 and MgH_2 shown in Fig. 6(a) illustrate that the major energy loss peak is occurring at 5.6 eV for CaH_2 and for MgH_2 it is 13.28 eV, these values corresponds to edge of plasma energy. Our value in case of MgH_2 is in good agreement to the experimental measured value of Paik et al [43], which was found to be 14.8 eV. These peak positions which correspond to plasma frequency show the transition from semiconductor to dielectric character of a material.

An essential optical parameter i.e. reflectivity spectra $R(\omega)$ shown in fig 6(b) is obtained by using imaginary and real parts of dielectric function, it is clearly observed that these hydrides acquire little reflectivity at low value of energies. It then start increasing at 2.1 eV for both materials then an increase in the reflectivity occurs at high energy levels for CaH_2 and a rapid increase occurs for MgH_2 at the intermediate and high energy levels. From Fig. 6(b) it is also clearly observed that transition in-between the bands take place mostly in the (3–13) eV of energy ranges for these the two materials. At higher energies in the region of 13.2 eV for CaH_2 and MgH_2 respectively some strong reflectivity maximum peaks are observed which mostly arise due to inter band transitions. The extinction coefficient shown in the Fig. 6(c) gives knowledge about all the linear optical properties and the absorption of light and its characteristics at band edges. The inter band transition from valence band to conduction band of electrons are responsible for the observed peaks in the illustrated extinction coefficient $k(\omega)$. We observed curves of greater magnitude in the extinction coefficient *k(ω)* for photon energies in the range of 2.5 eV to 10 eV for both the materials.

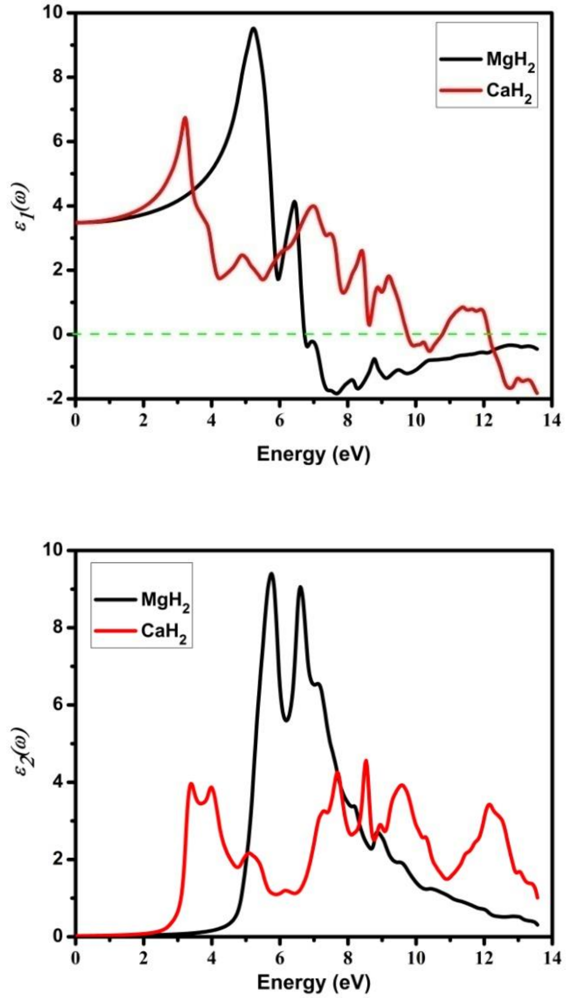


Fig. 4(a) and 4(b): The frequency dependent Real and Imaginary parts ($\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$) of dielectric functions of MgH_2 and CaH_2.

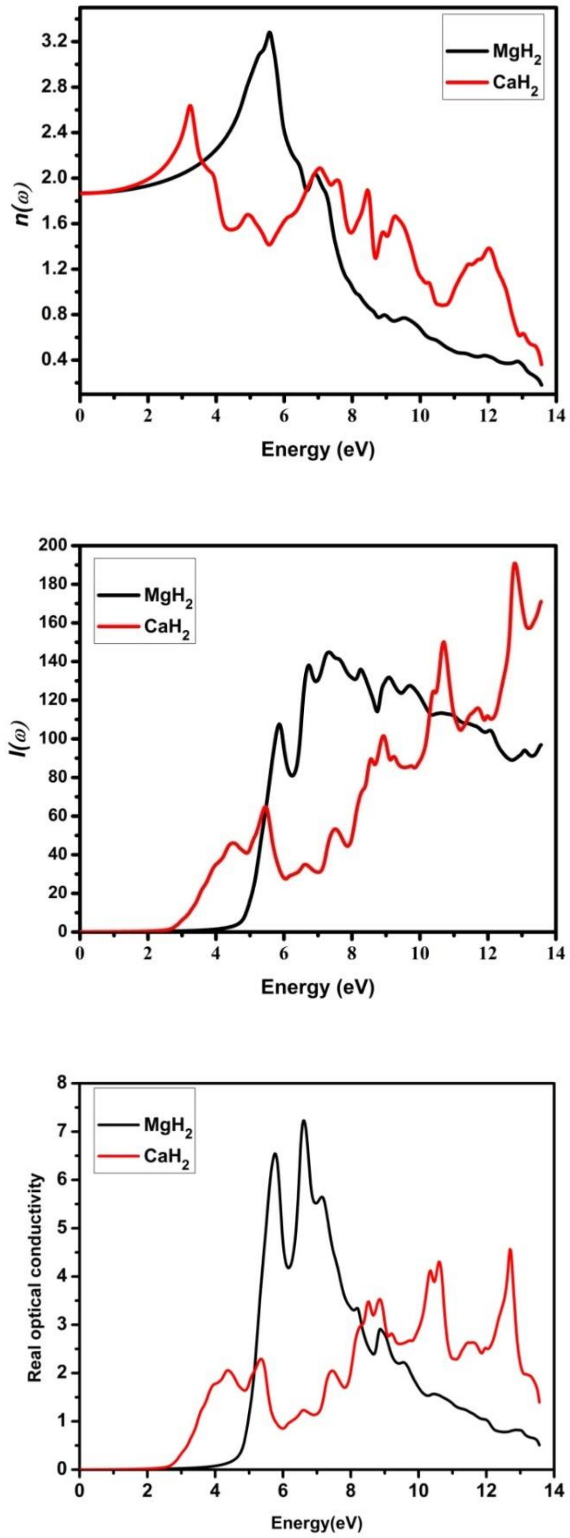
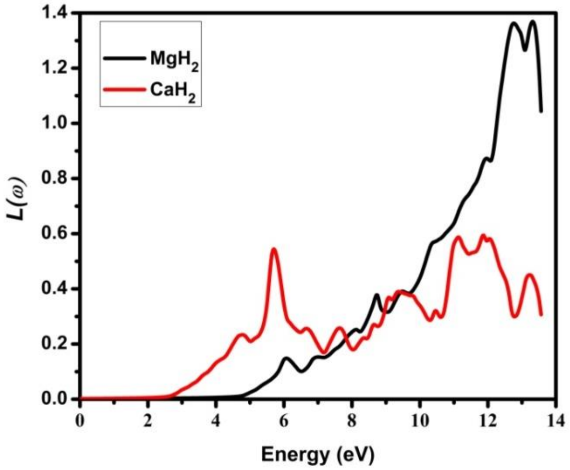


Fig. 5(a), 5(b), 5(c): Frequency dependent Refractive index *n(ω)*, absorption coefficient *I(ω)* and Real part of optical conductivity.


MgH$_2$
CaH$_2$
L(ω)
Energy (eV)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
2
4
6
8
10
12
14

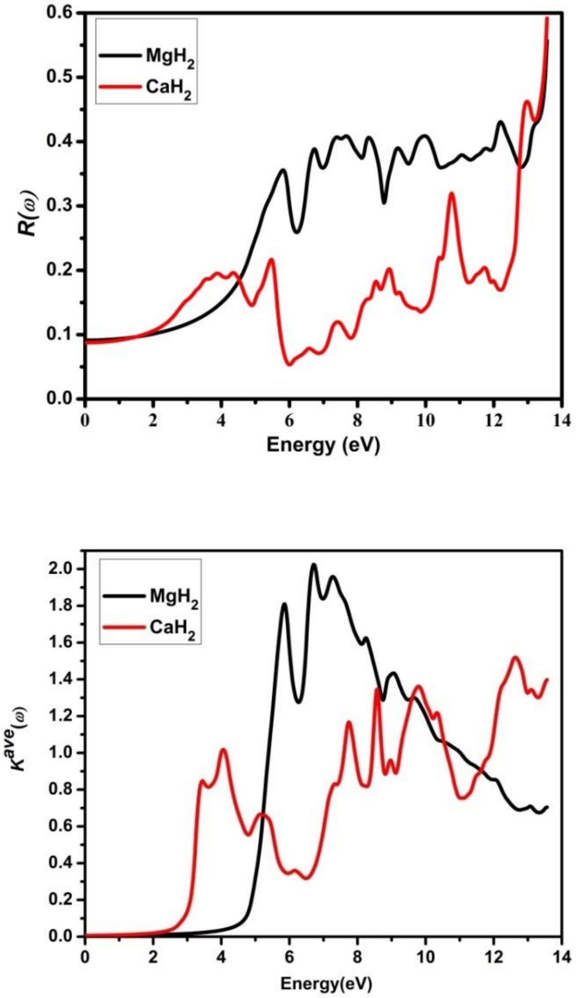


Fig. 6(a), 6(b), 6(c): The frequency dependent Energy loss function *L(ω)*, Reflectivety *R(ω)* and Extinction coefficient *k(ω)* for MgH_2 and CaH_2 materials.

4. Conclusion

In summary the detail information about the electronic and optical properties of MgH_2 and CaH_2 materials are investigated by using first principles calculations with GGA potential. Our calculated band gap values which are reported to be 4.91 eV and 2.01 eV for MgH_2 and CaH_2 respectively were in good agreement in comparison to the other theoretical and experimental values, our band gap values for both these materials indicates that these two hydrides are insulators. The band structure and density of states calculation also indicates the presence of ionic bonding in case of MgH_2. Among these two metals hydrides, MgH_2 being most intensely investigated to exploit its potential usage as H_2 energy carrier and also expanded its importance its applications in optical switching. So the optical characteristics are deeply explored to get improved application status of these materials, we therefore calculated the real and imaginary parts of the complex dielectric function, absorption and extinction coefficient, refractive index, reflectivity spectra, real part of optical conductivity and the energy loss function which is a function of photon energy and further compared and discussed our results with that of literature. A larger anisotropy which is in the real part $\varepsilon_1(\omega)$ and in the imaginary part $\varepsilon_2(\omega)$ of dielectric function for these two compounds closer to the main peak is observed. Similarly the calculated absorption coefficient spectrum in the observed energy range confirms the two materials as promising candidates for optoelectronic devices.

References

[1] S.Takagi, S.I Orimo, Recent progress in hydrogen-rich materials from the perspective of bonding flexibility of hydrogen. Scr. Mater. (2015), 109, 1–5.

[2] L. Schlapbach, A. Zuttel, Hydrogen-storage materials for mobile applications. Nature (2001), 414, 353–358.

[3] U. Eberle, M. Felderhoff, F. Schüth, Chemical and physical solutions for hydrogen storage. Angew. Chem. Int. Ed. (2009), 48, 6608–6630

[4] K. Yoshimura, C. Langhammer, B. Dam, Metal hydrides for smart window and sensor applications. MRS Bull. (2013), 38, 495–503

[5] M.V. Lototskyy, V.A. Yartys, B.G. Pollet, R.C. Bowman, Metal hydride hydrogen compressors: A review. Int. J. Hydrog. Energy (2014), 39, 5818–5851

[6] M. Felderhoff, B. Bogdanovic, High temperature metal hydrides as heat storage materials for solar and related applications. Int. J. Mol. Sci. (2009), 10, 325–344.

[7] R.Mohtadi, S. Orimo, The renaissance of hydrides as energy materials. Nat. Rev. Mater. (2016), 2, 16091.

[8]A. Unemoto, M. Matsuo, S. Orimo, Complex hydrides for electrochemical energy storage. Adv. Funct. Mater. (2014), 24, 2267–2279.

[9] Y. Oumellal, A. Rougier, G.A. Nazri, J.M. Tarascon, L. Aymard, Metal hydrides for lithium-ion batteries. Nat. Mater. (2008), 7, 916–921.

[10] I.P. Jain, C. Lal, A.Jain, Hydrogen storage in Mg: A most promising material. Int. J.Hydrogen Energy (2010), 35, 5133–5144.

[11] S. Djellab, Y. Bouhadda, M. Bououdina, N. Fenineche and Y. Boudouma, Elec. Mater, vol. (2016), 45, no. 8.

[12] J.P. Bastide, B. Bonnetot, J.M. Letoffe, and P. Claudy, Mater. Res. Bull. (1980), 15, 1215
[13] M. Bortz, B. Bertheville, G. Bottger, and K. Yvon, J. Alloys Compd. (1999), 287, L4.

[14] Y. Bouhadda, A. Rabehi, and S. Bezzari-Tahar-Chaouche, Revue des Energies Renouvelables. (2007), 10, 545

[15] SZh Karazhanov, A.G. Ulyashin, P. Vajeeston, and P. Ravindran, Philos. Mag. (2008), 88, 2461

[16] B. Pfrommer, C. Elsesser, and M. Fahnle, Phys. Rev. B, (1994), 50, 5089

[17]U. Haussermann, H. Blomqvist, and D. Noreus, Inorg. Chem. (2002), 41, 3684

[18] G. Krasko, Metal-Hydrogen Systems Pergamon, New York, (1982), p. 367.

[19] Z.X. He and W. Pong, Phys. Scr. (1990), T41, 930

[20] J. Isidorsson, I. A. M. E. Giebels, H. Arwin and R. Griessen Physical Review B (2003), 68, 115112

[21] P. van der Sluis, M. Ouwerkerk, and P.A. Duine, Appl. Phys. Lett. (1997), 70, 3356

[22] D. P. Sveinbjörnsson, D. Blanchard, J. S. G. Mýrdal, R. Younesi, R. Viskinde, M. D. Riktor, T. Vegge, Ionic conductivity and the formation of cubic CaH_2 in the $LiBH_4$-$Ca(BH_4)_2$ composite. Journal of Solid State Chemistry, (2014), 211, 81-89

[23] H. F. Franzen, J. Memck, M. Umana, A. S. Khan, D. T. Peterson, I. R. McCwxy and R. J. Thom I. Electron Specrrosc. Rehr. Phenom. (1977), 11 439

[24] K. Yamamoto, K. Higuchi, H. Kajioka, H. Sumida, S. Orimo, and H. Fujii, J. Alloys Compd. (2002), 330-332, 352

[25] F.H. Ellinger, J.C.E. Holley, B.B. McInteer, D. Pavone, R.M. Potter, E. Staritzky, and W.H. Zachariasen, J. Am. Chem. Soc. (1955), 77, 2647

[26] P. Balaha, K. Shewartz, G.K.H. Madsen, D. Kvsnicka, J. Luitz. WIEN2K, an augmented plane wave+local orbitals program for calculating crystals properties. Wien, Austria: Karlheinz Schewartz, Techn. Universitat; (2001), ISBN 3-9501031-1-2.

[27] E. Akiba, Hydrogen-absorbing alloys. Curr Opin Solid State Mater (1999), 4:267-72

[28] P. Vajeeston, P. Ravindran, R. Vidya, H. Fjellvag, A. Kjekshus, Pressure-induced phase of $NaAlH_4$: a potential candidate for hydrogen storage, Appl Phys Lett (2003) 82:2257-64.

[29] S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, A.P. Sutton, Phys. Rev. B 57 (1997) 1505

[30] F. Spadavecchia, G. Cappelletti, S. Ardizzone, M. Ceotto, L. Falciola, J. Phys. Chem. C 115 (2011) 6381

[31] R. Long, N.J. English, Chem. Phys. Lett. 498 (2010) 338.

[32] J. Sun, H. Wang, J. He, Y. Tian, Phys. Rev. B 71 (2005) 125132

[33] S. M. Baizaee, N. Mousavi, Physica B 404 (2009) 2111.

[34] H. Damany, P. Laporte, Opt. Commun. 16 (1976) 272.

[35] Z. Zhou, M. Li, L. Guo, J. Phys. Chem. Solids 71 (2010) 1707.

[36] A. C. Switendick, Solid State Commun. (1970), 8 1463

[37] D. I. Peterman, B. N. Harmon and Marehiando 1 (1979) Phys. Rev. B 19 4867

[38] S. Ameri Phys. Rev. B (1981), 23 4242

[39] J. H. Weaver, M. Gupta, and D. T. Peterson, Solid State Commun. (1984), 51, 805

[40] R. Yu and P. Lam Phys. Rev. B, (1988), 37, 8730

[41] R. Ahmed et al, Comput. Mater. Sci. (2007), 39, 580

[42] F. Wooten, Optical Properties of Solids (New York: Academic press), (1972), ch 5

[43] B. Paik, A. Walton, V. Mann, D. Book, I. P. Jones and I. R. Harris Appl. Phys. Lett. (2012), 100 193902

[44] P. Vajeeston, P. Ravindran, A. Kjekshus, and H. Fjellva˚g, Phys. Rev. Lett. (2002), 89, 175506

[45] L.G. Hector, J.F. Herbst, W. Wolf, P. Saxe, and G. Kresse, Phys. Rev. B (2007), 76, 014121