A DFT Study of Two New Hypothetic Brucite-Like Structures: $Mg(XH)_2$ (X = S, Se)

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Received: 24.09.2024 & Accepted: 17.01.2025

Doi: 10.12693/APhysPolA.147.98

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Guided by the potential applicability of multifunctional magnesium hydroxide in various technological and medical applications, the present work consists of studying the physical properties of the brucite $Mg(OH)_2$ and the prediction of two new hypothetic brucite-like materials, referred to as $Mg(SH)_2$ and $Mg(SeH)_2$. According to our results, both $Mg(SH)_2$ and $Mg(SeH)_2$ have very good chemical, mechanical, and dynamic stability, which promotes the possibility of their synthesis. In addition, we observed a clear correction of the band gap that fits well with experimental results from the literature. Moreover, the value of the gap decreases by substituting the atoms of oxygen with those of sulphur and selenium. Both tested materials also exhibit crystalline anisotropy, high transparency in the visible range, and high absorption and significant photoconductivity in the ultraviolet spectral region, suggesting their potential use in solar cells as buffer layer and a variety of technological applications.

topics: brucite, 2D materials, transparent semiconductors

1. Introduction

First-principles calculations using density functional theory (DFT) have become an essential tool for modelling and predicting structural, electronic, magnetic, and elastic properties of the most complex materials or systems. DFT is also a tool of choice for predicting new materials, modelling them, or conducting virtual experiments, which can predict the physical and/or chemical properties of materials when the actual experience is lacking or is very expensive and sometimes difficult to achieve. Furthermore, simple or complex materials constitute all the devices and objects that surround us. The choice and combination of certain materials makes it possible to combine several interesting physical properties. The synthesis and prediction of new multifunctional and ecological materials are at the heart of the work currently carried out around the world. Magnesium is one of the most abundant non-toxic metals in the Earth's crust. It forms the basis of the structure of magnesium hydroxide $Mg(OH)_2$. Brucite $Mg(OH)_2$ is a multifunctional material with numerous technological applications [1], such as in pharmaceuticals, biomedicine [2, 3], absorbers [4], optoelectronic devices, and energy technology as a buffer layer in solar cells [5, 6], etc.

The sulphur and selenium atoms are in the same chalcogen family (group 16) as oxygen. They have 6 valence electrons, leaving two electrons to fill the outer shell; moreover, their most common oxidation states with oxygen are ± 2 . We have imagined and assumed that if we replace the oxygen sites in the structure of $Mg(OH)_2$ with those of sulphur and selenium, we will surely obtain new crystalline structures with the same physical characteristics as brucite. With this in mind, first, we undertook a complementary and enriching study of the physical properties of $Mg(OH)_2$ and collected the experimental and theoretical results prior to our work. Secondly, we have extended the study of the two predicted new brucite-like materials, namely $Mg(SH)_2$ and $Mg(SeH)_2$, by the theoretical analysis of their structural, optoelectronic, elastic, and dynamical properties, comparing them with those of brucite $(Mg(OH)_2)$.

In this study, we used the non-local screened exchange functional (sX-LDA) to explain the electronic structure. This approach has been supported by several scientists [7–9], who have demonstrated that the results obtained using it perfectly reflect those obtained by experimental methods, especially since it accurately corrects the error of the optoelectronic properties compared to other functionals (LDA — local-density approximation, GGA — generalized gradient approximation, etc.), in particular A DFT Study of Two New Hypothetic Brucite-Like...

Structural			$Mg(SH)_2$	$Mg(SeH)_2$					
$\operatorname{parameters}$	sX-LDA	PBE^{a}	$HSE06^{a}$	HF^{b}	Exper. ^c	$\operatorname{Exper.}^{d}$	Exper. ^e	sX-LDA	sX-LDA
a = b [Å]	3.147	3.189	3.126	3.148	3.148	3.150	3.142	3.926	4.176
c [Å]	4.765	4.773	4.730	5.263	4.779	4.770	4.766	5.524	6.017
c/a	1.514	1.497	1.513	1.672	1.507	1.514	1.517	1.407	1.441
V [Å ³]	40.877	42.02	40.04	45.20	41.01	40.99	40.75	73.75	90.87
$ ho~[{ m g/cm^3}]$	2.370	_	_	_	2.360	_	2.38	2.036	3.37

Lattice constant values a and c, c/a, the volume V, and the density ρ of Mg(XH)₂, X = O, S, Se with $P\bar{3}m1$ space group.

^aRef. [18], ^bRef. [19], ^cRef. [20], ^dRef. [21], ^eRef. [22].



Fig. 1. $Mg(XH)_2$ trigonal crystalline lattice, with (X = O, S, and Se).

of the band gap energy. Several works strongly suggest the use of this approach, which is very well suited to the study of simple or complex crystalline systems [10, 11].

In this context, and because of the particular properties of magnesium hydroxide at the nanometric scale, the two hypothetical new materials $Mg(SH)_2$ and $Mg(SeH)_2$ studied in this work should arouse significant interest from researchers in the possible synthesis of these two new materials for new applications of this type of crystalline system.

2. Computational method

Throughout this study, all DFT calculations were undertaken using the Cambridge Serial Total Energy Package (CASTEP) codes [12]. All the optoelectronic properties were studied using the sX-LDA approach [7]. Moreover, the structural properties of these crystalline systems were calculated using the generalized gradient approximation (GGA) based on the Perdew–Burke–Ernzerhof (PBE) (GGA+PBE) approach [13]. The interaction between electrons and ions is described by the on-the-fly produced pseudo-potential method (OTFG). ultra-softWe used $Mg(OH)_2$ (Mg : 163.3 eV, O: 925.2 eV, H: 489.8 eV), Mg(SH)₂ (Mg : 900 eV, S: 650 eV. H: 650 eV), and $Mg(SeH)_2$ (Mg : 163.3 eV, Se: 1219.1 eV, H: 489.8 eV) as pseudo-potentials. A hybrid semi-local Tkatchenko and Scheffler (TS) approach [14] was used to correct the van der Waals (wdW) dispersion forces during calculations. For adequate accuracy, we selected the cut-off energy of 1020 eV, 990 eV, and 1350 eV for $Mg(OH)_2$, ${\rm Mg}({\rm SH})_2,$ and ${\rm Mg}({\rm SeH})_2,$ respectively. The special k-point meshes were $5 \times 5 \times 3$, with sampling integration over the Brillouin zone. The tolerances for an accurate geometry optimization have been set to the total energy of the system using a value of -5×10^6 eV/atom. Next, $F_{\rm max}$ was set below $0.01~{\rm eV}/{\rm \AA}$ for a pressure value of 0.02 GPa, and $D_{\rm max}$ was fixed at a value of -5×10^4 . The electronic configurations used in this work are: H: $1s^1$, Mg: [Ne] $3s^2$, O: [He] $2s^22p^4$, S: [Ne] $3s^23p^4$, and Se: [Ar] $4s^23d^43p^4$. The mechanical properties of the three structures were studied with the aid of elastic constants using the stress-strain method [15, 16]. The same elastic constants were used to estimate Debye and melting temperatures. All the properties were calculated based on the optimized crystal structures.

TABLE I

3. Results and discussion

3.1. Structural properties

The brucite, or Mg(OH)₂, is an inorganic compound belonging to crystalline layered systems which crystallize in the trigonal structure with space group $P\bar{3}m1$, N°164 (Fig. 1). Mg(OH)₂ primitive cell includes 5 atoms. The Wyckoff positions of Mg, O, and H, are, respectively, 1*a* (0, 0, 0), 2*d* (2/3, 1/3, 0.7818), and 2*d* (2/3, 1/3, 0.575) [17].

 $Mg(OH)_2$ and the brucite-like $Mg(XH)_2$ (X = S, Se) crystal structures are fully optimized by minimizing the total energy of the crystalline system as a function of the volume of the elementary cell, and we obtain the crystal lattice parameters at equilibrium (a, b, and c). We summarize the microstructural values calculated at zero Kelvin temperature in Table I. The values reported from experimental work and theoretical calculations are listed for comparison purposes [18-22]. For a proper interpretation of our results, we have taken into account the thermal effect on the crystal lattice occurring at room temperature. Table I shows that our $Mg(OH)_2$ calculated lattice parameters are practically the same as the experimental values. There are, however, some small differences from other theoretical works, which are slightly influenced by the different functionals used in each calculation. It is indicative of an anisotropy of bond forces in the $Mg(OH)_2$ lattice. Note that the dispersion of the results is also due to equations of state (EOS) used in each calculation. Moreover, from Table I, it follows that when substituting the oxygen atoms in the $Mg(OH)_2$ matrix with the S and Se atoms, the parameters of the other two new compounds are higher than those of $Mg(OH)_2$. This is clearly due to the size of the sulphur and selenium atoms compared to those of oxygen, which are of the order of $R_{\rm O} = 0.65$ Å, $R_{\rm S} = 1.09$ Å, and $R_{\rm Se} = 1.22$ Å.

3.2. Mechanical and thermal properties

Many technological applications are closely linked to the mechanical properties of materials, such as fracture toughness, solid stability, bending under load, internal deformation, thermoelectric stress, ductility, and brittleness. Moreover, the durability and synthesis of a material is indisputably linked to its stability [23–26].

The trigonal crystalline structure with the space group $P\bar{3}m1$ (N°164) has elastic constants (C_{ij} [GPa]) given by the relation [27, 28]

$$C_{ij} = \frac{1}{V_0} \left(\frac{\partial^2 E}{\partial \varepsilon_i \partial \varepsilon_j} \right),\tag{1}$$

where E is the total energy, V_0 is the volume, and ε_i and ε_j are the strains.

We have summarized in Table II all the mechanical constants and other theoretical and experimental results [13, 18, 24–33]. Moreover, we have also shown in Table II the calculated elastic constants for Mg(SH)₂ and Mg(SeH)₂. We observe that some elastic constant values are slightly higher than in other works, which is due to the different approaches used, but the principle remains the same, particularly for bulk modulus and anisotropy indices. Moreover, the mechanical constants of Mg(SH)₂ and Mg(SeH)₂ are much lower than those of Mg(OH)₂, which is mainly due to the substitution of oxygen by sulphur and selenium, as well as to the differences in the binding forces between the atoms of each crystal structure. In addition, the value of the acoustic anisotropy index is virtually the same for all three compounds, showing the same anisotropy character.

In our case, the necessary and sufficient conditions for the mechanical stability of our crystal systems must satisfy the following equations

$$C_{66} = 1/2 (C_{11} - C_{12}), \qquad C_{11} > |C_{12}|,$$

$$2C_{13}^2 < C_{33}(C_{11} + C_{12}), \qquad C_{44} > 0,$$

$$2C_{14}^2 < C_{44} (C_{11} - C_{12}) \equiv C_{44}C_{66} .$$

(2)

Table II clearly shows that the Born-Huang stability criteria have been met, confirming the mechanical stability of the two new brucite-type materials [28, 34]. The elastic constants of stiffness C_{ij} are related to several mechanical and thermal properties of the solids such as the linear compressibilities $\chi_{a,b}$, χ_c along the axes a and c, and the compressibility of the volume χ by the following relations [34, 35]

$$\chi_{a,b} = \frac{1}{a} \left. \frac{\partial a}{\partial p} \right|_{p=0} = \frac{C_{33} - C_{13}}{C_{33} \left(C_{11} + C_{12} \right) - 2C_{13}^2}, \quad (3)$$

$$\chi_c = \frac{1}{c} \left. \frac{\partial c}{\partial p} \right|_{p=0} = \frac{C_{11} + C_{12} - 2C_{13}}{C_{33} \left(C_{11} + C_{12} \right) - 2C_{13}^2}, \qquad (4)$$

$$\chi = \frac{1}{V} \left. \frac{\partial V}{\partial p} \right|_{p=0} = 2\chi_{a,b} + \chi_c.$$
(5)

Generally, anisotropic materials have some microstructural shear weaknesses, such as microcracks [35, 36]. For this reason, we calculated the shear anisotropy parameters along the shear plane (100) or (010) between directions [011] or [101] and [010] or [001], using the following relation [37]

$$A_{a,b} = \frac{4C_{44}}{(C_{11} + C_{33} - 2C_{13})},\tag{6}$$

and for (001), the shear plane between [110] and [010] directions, using

$$A_c = \frac{2C_{66}}{(C_{11} - C_{12})}.$$
(7)

Table II shows that for $Mg(XH)_2$ (X = O, S, and Se), the values of the ratio of elastic constants $\frac{C_{11}}{C_{33}}$ and $\frac{C_{12}}{C_{13}}$ are > 1, $\frac{C_{44}}{C_{66}}$ is < 1, and the linear compressibility $\frac{\chi_{a,b}}{\chi_c}$, as well as the shear anisotropic factor $\frac{A_{a,b}}{A_{a}}$, are less than 1 — this indicates that the compounds present an anisotropic elastic behaviour. Therefore, a slight elastic anisotropy in compression and shear characterizes the brucite phase of the $Mg(XH)_2$ compounds. Moreover, the linear compressibility value χ_c is slightly larger than $\chi_{a,b}$, which shows that the (001) plane is more difficult to compress than the (100) or (010) plane this affirms the fact that the value of the elastic constant C_{11} is slightly larger than that of C_{33} . At the same time, the value of $A_{a,b}$ is slightly smaller than that of A_c , indicating that the anisotropy of the (100) and (010) planes is more pronounced than that of the (001) plane.

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TABLE II

$A_a = C_{33}/C_{11}.$										
Elastic			$Mg(OH)_2$			$Mg(SH)_2$	$Mg(SeH)_2$			
constants	sX-LDA	$GGA-PBE^{a}$	Exper. ^b	$\operatorname{Exper.}^{c}$	Exper. ^{c,*}	sX-LDA	sX-LDA			
C_{11}	166.2	156.3	156.7	159.0	154.0	61.21	56.77			
C_{12}	44.15	45.0	44.4	43.3	42.1	31.70	31.51			
C_{13}	8.5	10.1	12.0	11.1	7.8	5.04	6.44			
C_{33}	62.83	50.4	46.3	49.5	49.7	24.02	21.46			
C_{44}	25.7	21.8	21.7	22.8	21.3	12.96	11.70			
C_{66}	61.03	55.7	56.2	57.9	55.95^{\bullet}	14.75	14.85			
C_{14}	1.78	0.2	_	_	1.3	-1.19	-1.28			
$\chi_{a,b}$	0.004	0.004^{ullet}	0.0038•	0.0039^{\bullet}	0.0043^{\bullet}	0.0087	0.0078			
χ_c	0.015	0.018^{\bullet}	0.019^{\bullet}	0.018^{\bullet}	0.018^{\bullet}	0.038	0.041			
χ	0.023	0.026^{\bullet}	0.027^{\bullet}	0.026^{\bullet}	0.027^{\bullet}	0.055	0.057			
$A_{a,b}$	0.485	0.467^{\bullet}	0.485^{\bullet}	0.489^{\bullet}	0.453^{\bullet}	0.69	0.671			
A_c	1.0	1.0^{\bullet}	1.0•	1.0^{\bullet}	1.0^{\bullet}	1.0	1.0			
B_H	50.4	46.4	51.0 ± 04.0^{d}	54.3 ± 1.5^{e} 47.0 ± 5.0^{f}	31.3	21.8	21.02			
G_H	40.6	35.4	_	_	35.2	14.45	12.64			
$ u_H$	0.18	0.20			—	0.23	0.25			
H_H	9.91	—				3.82	3.11			
Y_H	96.02	84.7				35.52	31.60			
A_Z	0.42	0.39^{\bullet}	0.38•	0.39•	0.38^{\bullet}	0.88	0.79			
A_a	0.37	0.32^{\bullet}	0.29•	0.31^{\bullet}	0.32^{\bullet}	0.39	0.38			
C_{11}/C_{33}	2.64	3.10^{\bullet}	3.38●	3.21^{\bullet}	3.10^{\bullet}	2.55	2.64			
C_{12}/C_{13}	5.19	4.45^{\bullet}	3.70●	3.90^{\bullet}	5.39^{\bullet}	6.29	4.89			
C_{44}/C_{66}	0.42	0.39^{\bullet}	0.38•	0.39^{\bullet}	0.38^{\bullet}	0.87	0.92			
$A_{a,b}/A_c$	0.28	0.22^{\bullet}	0.19•	0.21^{\bullet}	0.23^{\bullet}	0.23	0.20			
$\chi_{a,b}/\chi_c$	0.48	0.46^{ullet}	0.48•	0.49^{\bullet}	0.45^{\bullet}	0.69	0.71			

The summarized values of elastic constants C_{ij} , linear and volume compressibility ($\chi_{a,b}$, χ_c , and χ [TPa⁻¹], shear anisotropic factor ($A_{a,b}$ and A_c), bulk modulus B [GPa], shear modulus G in the Voigt–Reuss–Hill approximation, Young modulus Y, Poisson ratio ν , hardness H, the Zeener anisotropy index A_Z , and the acoustic anisotropy $A_a = C_{33}/C_{11}$.

(•)indicates values from our calculations.

^(*)indicates results of the adjustment to Eulerian finite strain equations.

^aRef. [13, 18], ^bRef. [24, 29], ^cRef. [25, 30], ^dRef. [26, 31], ^eRef. [27, 32], ^fRef. [28, 33]

Generally, the shear modulus (G) characterizes its deformation resistance due to shear stress and rigidity of a material. Therefore, the shear modulus (G) and the shear modulus (B) of Mg(XH)₂ (X = O, S, and Se) were calculated using the Voigt, Reuss, Hill [38–40] approximation method, which is more accurate and reflects the experimental values well.

Moreover, the brittleness or ductility of materials can be assessed by the bulk modulus and the shear modulus ratio, i.e., B_H/G_H . Pugh [41] has shown in his work that when $(B_H/G_H) > 1.35$, the material's ductility is improved and that the material is fragile for $(B_H/G_H) < 1.35$. Indeed,

the (B_H/G_H) values are 1.24, 1.50, and 1.66 for Mg(OH)₂, Mg(SH)₂, and Mg(SeH)₂, respectively, showing that Mg(S/SeH)₂ are more brittle materials than Mg(OH)₂. Young's Y module reflects the ability of materials to resist deformation, i.e., Young's modulus Y indicates that the material has high rigidity and is not easily deformed. (Mg(XH)₂ (X = O, S, Se) Young's modulus values along x and y ($Y_x = Y_y = 153.67, 44.28, 38.55$ GPa) and z ($Y_z = 62.14, 23.47, 20.52$ GPa) axes demonstrates that the compounds have a consistent rigidity and hardness, which is a consequence of their anisotropy.

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TABLE III

Summarized values of elastic Debye temperature $\theta_{\rm D}$, average sound velocity v_m , melting temperature T_m , minimum thermal conductivity $\kappa_{\rm min}$, final formation enthalpy H_F , entropy S, and heat capacity C_V of Mg(XH)₂ (X = O, S, Se).

Compound	θ_{D}	v_m	T_m	$\kappa_{ m min}$	$S \; [\mathrm{J/(mol \; K)}]$	$C_V [\mathrm{J/(mol \ K)}]$	H_F
Compound	[K]	[m/s]	[K]	W/(m K)]	(at 298 K)	(at 298 K)	$[\rm kJ/mol]$
$Mg(OH)_2$	646.67	4349.5	947.0	0.35	62.10	74.46	-1041.5
$Mg(SH)_2$	357.88	3023.9	573.7	0.21	114.33	92.87	-2184.1
${ m Mg(SeH)_2}$	240.62	2131.5	556.5	0.20	145.15	96.78	-6650.8

The Poisson's ratio (ν) gives an estimate of structural stability under stress. Indeed, $\nu > 0.26$ is observed for a ductile material, and $\nu < 0.26$ shows that our material is brittle [42]. The calculated ν values summarized in Table II confirm that our three materials are shear-stable. This shear stability is also confirmed by the calculated values of ν along the x, y and z axes which are represented by $\nu_{xy} = \nu_{xy} = 0.2614; 0.512; 0.543, \nu_{zx} =$ 0.0405; 0.054; 0.073 and $\nu_{xz} = \nu_{yz} = 0.10; 0.10; 0.13,$ $\nu_{zy} = 0.04; 0.054; 0.073.$

In general, the physical properties of a crystalline system are influenced by its anisotropy, which is characterized by Zener's and acoustic indices [43]

$$A_Z = \frac{2C_{44}}{(C_{11} - C_{12})}, \qquad A_a = \frac{C_{33}}{C_{11}}.$$
 (8)

The values of Zener's and acoustic indices must be equal to 1 for an isotropic material. On the other hand, when a material is anisotropic, the values of these indices are greater or less than 1. The crystalline anisotropy of our new materials is once again demonstrated by the values of the anisotropy index in Table II.

Understanding the thermal behaviour of materials is a necessary condition for accessing technological applications. Debye's temperature $\theta_{\rm D}$ is among the most important thermal properties. Generally, $\theta_{\rm D}$ characterizes the behaviour of thermal capacity and hardness of solids. It also links the material's mechanical properties to its melting temperature T_m and its minimum thermal conductivity $\kappa_{\rm min}$. Therefore, $\theta_{\rm D}$ is estimated by [44]

$$\theta_{\rm D} = \frac{h}{k_{\rm B}} \frac{3n}{4\pi} \left(\frac{N_{\rm A}\rho}{M}\right)^{1/3} v_m,\tag{9}$$

where $N_{\rm A}$ is Avogadro's number, h and $k_{\rm B}$ are Planck's and Boltzmann's constants, ρ is density, M is molecular mass, n is the number of atoms per unit cell, and v_m is the average sound's velocity defined as

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right]^{-1/3},\tag{10}$$

 with

$$v_t = \sqrt{G/\rho}$$
 and $v_l = \sqrt{(3B+4G)/(3\rho)}$ (11)

representing the transverse and longitudinal acoustic velocity, respectively. The melting temperature (T_m) of Mg(XH)₂ compounds is also calculated by [44]

$$T_m = 354 + \frac{4.5\left(2C_{11} + C_{33}\right)}{3}.$$
 (12)

From Table III, we can see that T_m values decrease when the oxygen atom in the brucite-like crystalline structures is replaced by the sulphur and selenium atoms.

In general, the thermal conductivity decreases with increasing temperature up to a limiting value known as the minimum thermal conductivity, which is subject to an intrinsic limit that depends on phonon dispersion. In order to verify the thermal performance of our materials, we calculated this entity using Cahill's approach, which is based on the wave speed of the crystal lattice vibrations [45]

$$\kappa_{\min} = \frac{k_{\rm B}}{2.48} n^{2/3} \left(2v_t + v_l \right). \tag{13}$$

From Table III, we can note that $\theta_{\rm D}$ and $\kappa_{\rm min}$ decrease when the oxygen atom in the brucite crystalline structure is replaced by the sulphur and selenium atoms, suggesting that Mg(S/SeH)₂ are less hard than Mg(OH)₂.

After checking the mechanical stability of our materials, we also examined their chemical or thermal stability by calculating the formation enthalpy or heat of formation of a compound, which is the change in enthalpy when a mole of a substance is formed from its constituent elements in their most stable state. In general, a material that does not decompose when exposed to heat is a thermally stable material. Consequently, a more negative enthalpy of formation will correspond to more stable compounds, and its thermal stability is higher. From Table II, we can clearly see that our similar to brucite structures have negative enthalpies, which means that the compounds are thermally stable. No experimental and/or theoretical data comparable to our results were found in the literature.

In general, three-dimensional (3D) solids have a specific thermal dependence to very low temperatures proportional to T^3 in the form $C_v \propto (T/\theta_{\rm D})^3$. This dependence is described by the relationship [15]

$$C_v = \frac{12\pi^4}{5} n k_{\rm B} \left(\frac{T}{\theta_{\rm D}}\right)^3 = 234 \left(\frac{T}{\theta_D}\right)^3 n k_{\rm B} \,. \tag{14}$$



Fig. 2. Variation of heat capacity $C_v versus(T/\theta_{\rm D})$, (inset: log-log plot of $C_v(T/\theta_{\rm D})$).

Figure 2 shows the lattice thermal capacity as a function of the reduced temperature $(T/\theta_{\rm D})$. Figure 2 (inset) clearly shows us that the Debye model for low-temperature solids is verified for our compounds.

3.3. Vibrational properties

Lattice vibration modes of a crystalline system play a central role in determining its thermal, electronic, and optical properties. Figure 3 shows the phonon dispersion curves with longitudinal optical– transverse optical (LO-TO) splitting. We can see that there are no negative frequencies (imaginary phonon) in the entire Brillouin zone, suggesting the good dynamic stability of our materials in their brucite-type structure. The corresponding total and partial projected phonon density is shown in Fig. 4.

The trigonal primitive cell of the brucite structure has 5 atoms. The group theory predicts, in this case, 15 modes of vibration or degrees of freedom described by the following irreducible representation for the acoustic and optical modes at the Brillouin zone centre. Three of them are acoustic, and the rest of the other modes are optical [46, 47], so

$$\Gamma = 2A_{1g} \oplus 2E_g \oplus 3A_{2u} \oplus 3E_u. \tag{15}$$

Since the brucite structure has an inversion centre, and taking into account the mutual exclusion rule, we will have four symmetric A_{1g} and E_g modes that are active in Raman and four anti-symmetric A_{2u} and E_u modes that are active in infrared, and E modes are doubly degenerated. In addition, the Mg ions are located in the inversion centre, hence



Fig. 3. Phonon dispersion spectra (with LO-TO splitting).

they do not participate in any of the active Raman modes whose normal coordinates are symmetric to the inversion symmetry operation, but in order to preserve the mass centre of the structure, they participate in infrared (IR) modes.

Figure 4, showing the total and partial density of phonon states, indicates that H atoms mainly contribute to the high-frequency optical region. On the other hand, the atoms of Mg, O, S, and Se are more dominant in the acoustic frequency region; this is mainly due to the mass differences of each species of atoms as well as the bond length of the Mg–X bond.

The calculated Raman and infrared spectra are shown in Fig. 5. We reported in Table IV [47–49] the values of all phonon frequencies and the apparent active modes of the calculated Raman and IR spectra (Fig. 5) and other calculated and experimental values found in the literature. According to the results of Mg(OH)₂, all active Raman and infrared modes values are in good agreement with previous theoretical and experimental data (see Table IV), indicating the effectiveness of our approaches used. Modes that involve the movement of hydrogen have their frequency lowered when the S and Se atoms replace the O atom in the brucite matrix. The difference in phonon frequencies between the

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Fig. 4. Phonon total density of states (TDOS) and partial density of states (PDOS) of $Mg(XH)_2$ (X = O, S, Se).

three compositions is entirely due to the different masses of the O, S, and Se atoms and the nature of their bond strength with the hydrogen atom.

We can note that the E_g mode related to displacements of O–H groups in the plane (001) at 269 cm⁻¹ moves to lower wavenumbers for S–H and Se–H at 143 and 87.7 cm⁻¹, respectively. The rocking movement of the atom H represented by $E_g(R)$ mode at 760 cm⁻¹ of Mg(OH)₂ shifts toward lower wavenumbers for Mg(SH)₂ and Mg(SeH)₂ at 499 and 448 cm⁻¹, respectively. The Mg(OH)₂ A_{1g} mode (breathing mode) at 434 cm⁻¹ also shifts to 237 and 145 cm⁻¹ for Mg(SH)₂ and Mg(SeH)₂, respectively. The Mg(OH)₂ high-frequency A_{1g}

TABLE IV

Phonon modes (at Brillouin zone centre, i.e., Γ point), Raman and infrared frequencies values, compared to the experimentally observed and theoretically calculated modes (units in cm⁻¹). Here, DFPT is density functional perturbation theory and PAW-PBE is the projector augmented wave method with Perdew–Burke–Ernzerhof (PBE).

Modes	Phonon frequencies		-	Raman frequ	Infrared frequencies					
					$Mg(OH)_2$					
	This work	DFPT^{a}	DFT^{b}	This work	$PAW-PBE^{c}$	$\operatorname{Exper.}^{d}$	This work	$PAW-PBE^{c}$	Exper. ^d	
E_g	268.80	265.66	268	269.6	269	280	_	_	_	
E_u (TO)	359.00	338.48	349	_	_	361	359.44	356	361	
E_u (LO)		382.62	375	_	_	416	_	416	416	
A_{2u}	474.38	480.29	487	_	_	461	474.26	438	461	
E_u (TO)	434.82	526.65	422	—	—	_	434.10	_	_	
E_u (LO)		703.21	727	_	_	_	_	_	_	
E_g	759.66	791.87	767	760	807	725	_	_	_	
A_{1g}	3727.83	3596.75	3686	3728	3411	3652	_	_	_	
A_{2u}	3764.66	3618.35	3727	_	_	3688	3765.23	3710	3688	
		Mg(SH) ₂								
E_{g}	143.34			143.4						
E_u (TO)	212.31			_		212.4				
E_u (LO)				_	-					
A_{1g}	237.31			237.4		-				
A_{2u}	290.38			_			290.12			
E_u (TO)	368.84			_			369.25			
E_u (LO)				_				_		
E_g	499.03			499		-				
A_{1g}	2591.04			2591		_				
A_{2u}	2601.52			_			2602			
	Mg(SeH) ₂									
E_g	87.84			87.80				_		
E_u (TO)	181.11			_				181.11		
E_u (LO)				_			_			
A_{1g}	144.92			145						
A_{2u}	242.35			_		242.5				
E_u (TO)	332.48			_				332.7		
E_u (LO)				_				_		
E_g	448.14			448.2				_		
A_{1g}	2297.23			2297				_		
A_{2u}	2307.90			_				2307.5		

^aRef. [48], ^bRef. [47], ^cRef. [18], ^dRef. [49]

mode at 3728 cm⁻¹ moves for Mg(SH)₂ and Mg(SeH)₂ at 2591 and 2297 cm⁻¹, respectively. On the other hand, the Mg(OH)₂ E_u modes linked to the parallel displacements of H atoms in the basal plane at 359 and 434 cm⁻¹ shift to (212, 290) and (181, 242) cm⁻¹ for Mg(SH)₂ and Mg(SeH)₂, respectively. Furthermore, the brucite A_{2u} mode at 474 cm⁻¹, which is due to the Mg sub-lattice

vibrations, moves for Mg(SH)₂ and Mg(SeH)₂ at 369 and 332 cm⁻¹, respectively. Finally, the stretch mode O–H represented by A_{2u} mode at 3765 cm⁻¹ shifts to 2602 and 2308 cm⁻¹ for S–H and Se–H, respectively. For more details on the dynamic properties of magnesium hydroxide, we invite the readers to consult the works of Reynard et al. [47], Lutz [50], and Duffy et al. [51].



Fig. 5. Calculated Raman (a) and infrared (b) spectra of $Mg(XH)_2$ (X = O, S, Se).

In general, the practical magnitude in vibrational spectroscopy is the wavenumber $\bar{\nu}$ [cm⁻¹], which depends on the reduced mass μ of the A–B system and the force constant k, which is proportional to the force of the covalent bond connecting the masses m_A and m_B of the bond, and it is expressed by the equation

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \tag{16}$$

with $\mu = m_A m_B / (m_A + m_B)$.

The decrease in vibration frequency was interpreted as being caused by hydrogen bridges or the increase in the bonding force of $\mathbf{O},\,\mathbf{S},\,\mathrm{and}\,\,\mathbf{S}\,\mathrm{e}\,\mathrm{ions}.$ In other words, the decreasing values of the frequencies are mainly due to the decrease in the binding constant force k and the increase in the reduced mass μ . Lutz et al. in their work [52] proposed that the vibrational frequency of the undisturbed OH⁻ ions at $3570 \pm 10 \text{ cm}^{-1}$ increases in ionic hydroxides due to the repulsion effects of the lattice, or decreases if hydrogen bonds are present, to a large extent up to 400 cm^{-1} in the case of common OH^{-} ...X bridges and only up to 70 cm^{-1} in the case of XH... OH^{-1} bonds. We note that the calculated O-H, S-H, and Se-H frequencies depend not only on the functional used but also on the pseudo-potential and the basis set [53].

3.4. Electronic properties

In order to correct the band gap value underestimated by the local-density approximation (LDA) and generalized gradient approximation (GGA) approaches, we have retained the advantages of LDA by introducing electron-electron interactions using the screen-exchange LDA functional [7, 54].

We present in Fig 6 the electronic band structures of $Mg(XH)_2$. We clearly observe that for the band structure calculated for $Mg(OH)_2$ using the GGA+PBE function (Fig. 6a) and comparing it to the sX-LDA approach (Fig. 6b). We notice a visible correction of the electronic structure of the conduction band due to non-local correlation effects. We also observe in Fig. 6 that near Fermi's level, valence-band structure maxima are not affected by non-local correlation effects. Moreover, the renormalization of the band gap energy due to the nonlocal correlation effects is characterized by the displacement of the minimum of the conduction band towards large energies. The corrections made by the sX-LDA approach to the values of the optoelectronic properties of materials, and especially to the band gap energy, have been reported in other studies [8–11].

Based on the upper parts of the valence band (VBM) and the lower parts of the conduction band (CBM) in Fig. 6, we can note that $Mg(XH)_2$ exhibits a direct band gap at the Γ -point, with



Fig. 6. $Mg(XH)_2$ (X = O, S, Se) electronic band structures.

a value of 6.81, 4.36 and 3.49 eV for Mg(OH)₂, Mg(SH)₂, and Mg(SeH)₂, respectively. Table V summarizes our computed band gap energies and theoretical and experimental values for Mg(OH)₂ found in literature, as well as those of the two new brucite-like compounds Mg(SH)₂ and Mg(SeH)₂ [18, 55–60]. We note from this table that the different values of the experimental band gap are dispersed from 5 to 7 eV [17, 55–60]. This decrease in E_g encourages the use of these two materials as semiconductors and in solar devices as buffers on copper indium gallium selenide (CIGS) solar cells [61].

We can notice a decrease in E_g for the other two brucite-like systems. On the other hand, we observe in Fig. 6 a densification of the electronic states of the conduction band by replacing oxygen with sulphur and selenium, which is linked to the electronic states of each atom.

We also note the perfect resemblance of the characteristics of the electronic states of the valence band for the three compounds, which is very clear in the density of states (DOS) curves presented in Fig 7, indicating the very nature of the covalent bond of chalcogen atoms with hydrogen.

Band gap energy of $Mg(XH)_2$ (X = O, S, and Se) (in [eV]) compared to experimental data and other DFT

TABLE V

Compounds	Methods	E_g [eV]
	This work (sX-LDA)	6.81
	$\mathrm{HSE06}^{a}$	7.30
	$\mathrm{HSE06m}^{b}$	7.70
	mBJ^b	7.16
	$G_3 W_0^b$	8.26
${\rm Mg(OH)_2}$	$\operatorname{Exper.}^{c}(\operatorname{thin}\operatorname{film})$	7.00
	DV-X α calculation ^c	7.00
	$\operatorname{Exper.}^{d}$ (nanodisks)	5.7
	$\operatorname{Exper.}^{e}$ (nanoparticles)	5.47
	$\operatorname{Exper.}^{f}$ (thin film)	5.17
	$Exper.^{g}$ (thin film)	5.8
$Mg(SH)_2$	This work (sX-LDA)	4.36
${\rm Mg(SeH)_2}$	This work (sX-LDA)	3.49

^aRef. [54], ^bRef. [18], ^cRef. [55], ^dRef. [56], ^eRef. [57], ^fRef. [58], ^gRef. [59]

calculations.



Fig. 7. Electronic TDOS and PDOS of $Mg(XH)_2$.

The calculated partial and total DOS are shown in Fig. 7. The overlap observed in Fig. 7 of the sand p states is a direct consequence of the hybridization sp^2 , which is predominant in the valence and conduction bands, which leads to the formation of covalent bonds between the atoms (O, S, and Se) and H. The strength of this hybridization is affected by the value of the state density, i.e., the covalent bond formed is stronger when more states are added to reinforce this hybridization. Figure 7a–c shows that for the three systems studied, the (VBM) is mainly provided by O-2p, S-3p, Se-4p orbitals, and the (CBM) is composed of major orbitals O-2p, S-3p, Se-4p and minor orbital H-1s. The upper part of the (VBM) (-4, 0 eV) is mainly provided by the O-2p, S-3p, Se-4p orbitals, and the lower part (-7, -4 eV) is provided by the O-2p, S-3p, Se-4p orbitals. In addition, there are significant contributions from Mg-2p and Mg-3s states to (VBM).



Fig. 8. Imaginary and real parts of the dielectric function of Mg(XH)₂.

There are also minor contributions of the H-1s and Mg-3s orbitals to the conduction band and a consistent contribution of the Mg-2p states to the conduction band. This confirms the claim that the outermost electrons of the chalcogen atoms (O, S, and Se) mainly affect the total DOS. The nucleus level is mainly composed of O-2s, S-3s, Se-4s and minority p-electrons [18, 62].

3.5. Optical properties

Generally, the anisotropic character of crystalline structures influences their physical properties, which gives them a wide range of possible features for new nanotechnologies. Optical properties are investigated for two polarization directions [100] $(\boldsymbol{E} \perp \boldsymbol{c}, \text{in-plane})$ and [001] $(\boldsymbol{E} \parallel \boldsymbol{c}, \text{out-of-plane})$ and in the photon energy range up to 35 eV. We note that depending on the direction of polarization of the incident electric field \boldsymbol{E} , the shapes and intensities of all the calculated optical spectra are different, indicating the anisotropy of these three crystal systems.

The degree of material polarization by an applied electric field **E** is estimated by the function $\varepsilon_1(\omega)$, and when this value is high, it implies an important capacity for polarization and energy storage. Conversely, the absorption, dissipation, or loss of energy is estimated by the function $\varepsilon_2(\omega)$, which is also related to the conductivity of the material [63, 64]. We have plotted the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the dielectric function in Fig. 8. The appearance of both dielectric functions clearly indicates a significant anisotropic behaviour. Indeed, the $\varepsilon_2(\omega)$ spectrum extremum values vary according to the different directions of polarization of E resulting mainly from the electronic transitions from the highest valence band states (H-p orbitals) to the lowest conduction band states (O-p, S-p, and Se-p).

We observe in Fig. 9 the effect of anisotropy of these brucite-like systems in the form of the spectrum $\alpha(\omega)$ following the directions of polarization of \boldsymbol{E} . Indeed, this effect is indicated by a large offset of $\alpha(\omega)$ between the directions of polarization $\boldsymbol{E} \perp \boldsymbol{c}$ and that of $\boldsymbol{E} \parallel \boldsymbol{c}$. We also notice a shift of the alpha spectra towards low energies for the compounds Mg(SH)₂ and Mg(SeH)₂ due to the different ions density.

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Fig. 9. (a) Absorption coefficient $\alpha(\omega)$. (b) Refractive index n. (c) Reflectivity R. (d) Loss function $L(\omega)$.

Similarly, the refractive index (Fig. 9b) is influenced by the structural anisotropy of these systems. The obtained values of static refractive index n(0)at $\omega = 0$ are virtually the same in both directions for each of the three brucite systems, indicating their high transparency in the visible region. Furthermore, the increase in the static refractive index value shown in Fig. 9b is due to the variation in density and compactness of the three systems.

Figure 9c shows the reflectivity spectra $R(\omega)$ of the Mg(XH)₂ systems. Microstructural anisotropy also influences this optical property. The spectra presented in Fig. 9a and c show that the reflectivity values are less than 3%, and those of the absorption coefficients are less than 1×10^4 cm⁻¹ in the visible region, suggesting high transparency in this spectral range.

Furthermore, the loss function $L(\omega)$, which characterizes the energy loss of an electron moving through a system, is depicted in Fig. 9d. We can see that $L(\omega)$ is accentuated in the ultraviolet range. Indeed, we estimated the values of the intense and acute peaks of $L(\omega)$ reaching the plasma frequency (12-32 eV)



Fig. 10. Two-dimensional (2D) representation of the ELF valence electrons distributions (iso-surface: ELF = 0.85) (a). ELF best fit (b). EDD plots $\delta \rho$ [eV/Å³] best fit (c).

for Mg(OH)₂, and (5–27 eV) for both compounds Mg(SH)₂ and Mg(SeH)₂. Plasma frequency values are 1.9 (26.3 eV), 3.97 (24.4 eV) in the [100] ([001]) polarization directions for Mg(OH)₂ and 4.8 (18.3 eV), 3.8 (19.1 eV) and 1.83 (16.6 eV), 3.35 (17 eV) for Mg(SH)₂ and Mg(SeH)₂, respectively. Note that $\varepsilon_1(\omega) = 0$, so it is cancelled out at plasma resonance; this is affirmed by the absence of $L(\omega)$ peaks in the high $\varepsilon_2(\omega)$ energy range. In other words, the $L(\omega)$ maximum is observed at the apparent plasma frequency ω_p and $\varepsilon_1(\omega) = 0$.

3.6. Charge distribution

3.6.1. Electron localization function (ELF)

The notion of the electronic location function (ELF) is a quantifiable explanation of Pauli's exclusion principle. Indeed, Becke and Edgecombe proposed "this indicator (ELF), which gives an estimate of the probability of finding two nearby electrons with the same spin, and describes the nature and visual information of the chemical bond" [65–67].

The three-dimensional (3D) ELF iso-surfaces in Fig. 10a visualize the electronic density of the X-H⁻ anion represented in terms of valence ELF iso-surface at 0.85. We clearly observe two regions (in vertical and in planar direction) of shared electronic interactions that form localized electron distributions of different shapes.

From Fig. 10b, showing the cross-section (2D), we can see the covalent nature of the bond between the two adjacent atoms X-H (X = O, S, and Se), which is indicated in the image by a strong electronic localization (0.5 < ELF < 1) that extends into the region between the two atoms. The region surrounding H has a $0.6 < ELF \le 1$, and for X atoms one has 0 < ELF < 0.3. This indicates that the electron location is higher around H than around X atom, clearly showing the ionicity of H by taking the necessary charge for the electronic equilibrium from the X atoms. Moreover, we note a small region between adjacent layers where 0 < ELF < 0.125, which is clearly empty, which is due to a very low electron density, suggesting the presence of van der Waals forces between the layers [18]. In addition, the strong covalent contribution to the X-H bond

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TABLE VI

Compound	Charge spilling	Species	Mulliken's atomic populations			Mulliken's charge	Formal ionic	Effective	Hirshfeld's	Effective valence
	[%]		s	p	Total	enarge	charge	varence	charge	valence
		Mg	0.33	0.42	0.75	1.25	2	0.75	0.35	1.65
$Mg(OH)_2$	0.63	0	1.83	5.15	6.99	-0.99	$^{-1}$	0.01	-0.29	0.71
		Н	0.64	0.00	0.64	0.36	0	-0.36	0.11	-0.11
$Mg(SH)_2$	0.74	Mg	0.48	0.61	1.09	0.91	2	1.09	0.24	1.76
		S	1.82	4.74	6.56	-0.56	-1	0.44	-0.15	0.85
		Н	0.90	0.00	0.90	0.10	0	-0.1	0.03	-0.03
		Mg	2.65	6.91	9.56	0.44	2	1.56	0.27	1.73
$Mg(SeH)_2$	0.39	Se	1.57	4.63	6.20	-0.20	$^{-1}$	0.80	-0.15	0.85
		Н	1.02	0.00	1.02	-0.02	0	-0.02	0.02	-0.02

Charge spilling parameter [%], orbital charges (electron (e^-)), atomic Mulliken's charge (e^-) , effective valence (e^-) , and Hirshfeld's charge (e^-) .

TABLE VII

Mulliken's bond number n^{μ} , bond overlap population P^{μ} , and bound length d^{μ} [Å] of Mg(XH)₂ (X = O, S, Se).

Compound	Bonds		This work		Other works			
Compound	Donas	n^{μ}	P^{μ}	d^{μ}	$d_{\mathrm{Exp}}{}^{a}$	${d_{\mathrm{Exp}}}^b$	$d_{ m DFT}$	
Mg(OH) ₂	H–O	2	0.64	0.961	0.953	0.958	0.950^{c}	
	H–O	2	0	2.411	—	_	_	
	H–H	1	-0.06	1.926	1.966	1.969	1.960^{c}	
	O-Mg	2	0.61	2.102	2.093	2.100	2.079^{c}	
	H–Mg	2	-0.30	2.711	—	_	—	
	H–S	2	0.74	1.352	1.328^{d}	—	1.350^{e}	
	H–S	2	-0.02	3.008	—	_	_	
$Mg(SH)_2$	H–H	1	-0.06	2.376				
	Mg-S	2	0.82	2.613				
	S–S	1	-0.36	3.377				
	H–Se	2	0.59	1.469	1.460^{f}	_	1.46^{g}	
	H–Se	2	-0.08	3.546				
${ m Mg(SeH)_2}$	H–H	1	0.01	2.680				
	Mg–Se	2	0.92	2.763				
	Se–Se	1	-1.02	3.552				

^aRef. [20], ^bRef. [21], cRef. [18], ^dRef. [72], ^eRef. [73], ^fRef. [74], ^gRef. [75]

is established along the c axis and is mainly due to the deep overlap of the valence orbitals of the O, S to Se atoms and hydrogen.

3.6.2. Electron difference density (EDD)

Electron difference density (EDD) indicates the difference between self-coherent valence charge density and the superposition of atomic valence densities. The contours of the electron density difference ($\delta\rho$ [eV/Å³]) are shown in Fig. 10c. Indeed, positive values $\delta\rho$ (> 0) indicate an electron gain, conversely negative values of $\delta\rho$ (> 0) imply a loss of electrons. Based on the standards of the colour scale

used, we observe that the contours of the O, S, and Se ions have negative values $\delta \rho < 0$, indicating a loss of electrons. Furthermore, the red contours between each X–H pair closer to each observed H ion indicate a large accumulation of electrons, i.e., $\delta \rho > 0$, which explains the covalent nature of the X-H bond. We also observe in Fig. 10c that electron transfer takes place from the interlayer region to the intralayer region, which is confirmed by the apparent loss of electrons in the inter-layer region and strengthens the X–H bond in the same plane, enhancing its chemical stability. Similarly, we see that the less positive hydrogen is strongly bound to the same anion X by the vertical covalent bond, hence the particular role of anion X in this type of crystalline system, i.e., constructing a transient site responsible for structural stabilization by maintaining two different chemical interactions with its electropositive partners within the Mg–X–H unit cell [18].

3.6.3. Population analysis

Another concept of electronic charge analysis was proposed by Mulliken in 1955 [68] and is based on the calculation of the distribution of electronic charges in a molecular structure, which leads us to the nature of the chemical bond between the atoms of the materials. In addition, there are other theoretical models explaining these same phenomena based on the density matrix, such as the models of Löwdin [69], Reed et al. [70], and Hirshfeld [71].

Tables VI and VII summarize calculated data. A high value of the bonding electron population indicates a high level of covalent nature, and a low value implicates a bond of ionic nature, while a zero value suggests a purely ionic bond. From Table VI, we observe that hydrogen atoms have a positive charge while X atoms (O, S, and Se) have negative charges, ensuring the transfer of charges from X atoms to H atoms (O: 0.99|e|, S: 0.56|e|, Se: 0.20|e|). This confirms the observations from the ELF and EDD calculations. We also note for Mg(SeH)₂ a slight transfer of charge from the atom H (0.02|e|).

On the other hand, based on the bond overlap population, P^{μ} values for the Mg(OH)₂ (H–O: 0.64, O–Mg: 0.61), Mg(SH)₂ (H–S: 0.74, S– Mg: 0.82), and Mg(SeH)₂ (H–Se: 0.59, Se–Mg: 0.92) bonds indicate a positive population and electron overlap that favours the covalent nature (see Table VII [18, 20, 21, 72–75]). Furthermore, the calculated values of the inter-atomic distances (X–H) are comparable to the experimental values found in the literature [18, 20, 21], demonstrating the precision of the approaches used in this work.

4. Conclusions

In conclusion, we report in this work new complementary results obtained using sX-LDA functional for well-understood magnesium hydroxide $Mg(OH)_2$ physical properties and the prediction of two new trigonal brucite-like materials, namely $Mg(SH)_2$ and $Mg(SeH)_2$. Our results show that $Mg(SH)_2$ and $Mg(SeH)_2$ are very stable chemically, mechanically, and dynamically, which promotes the possibility of their synthesis. $Mg(XH)_2$ (X = O, S, and Se) have a direct band gap at the Γ point, with values of 6.81, 4.36, and 3.49 eV, respectively, and exhibit crystalline anisotropy, high transparency, high absorption, and high photoconductivity spectra in the UV energy region. In addition, all brucite-type materials, $Mg(XH)_2$, have a pseudobidimensional character, since the strong bonding force is mainly covalent within the layers and less related to the weak (van der Waals-type) forces between the layers.

We can say that the current study is purely theoretical, but it is based on approaches and conditions that have proven themselves during these last decades and have been confirmed by experimental studies. We hope that the results obtained in this work will help stimulate other researchers to synthesize these DFT-predicted materials in order to confirm our results and obtain other interesting hidden physicochemical properties for possible technological applications.

Acknowledgments

We would like to thank Ms D. Bouchentouf for her support during the development of this study. I would also like to thank Professor Andreas ZEINERT of the Laboratoire de Physique de la Matière Condensée, Université de Picardie Jules Verne, Amiens, France, for his invaluable help.

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