http://dx.doi.org/10.35596/1729-7648-2021-19-8-92-98

Original paper

UDC 537.9

FIRST-PRINCIPLES STUDY OF STABILITY AND ELECTRONIC PROPERTIES OF SINGLE-ELEMENT 2D MATERIALS

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Submitted 9 December 2021

Abstract. We have estimated stability of single-element 2D materials (C_2, N_2, Si_2, P_2, Ge_2, As_2, Sn_2, Sb_2, Pb_2, and Bi_2) by *ab initio* calculations. The calculations of structural and mechanical properties of 2D materials were performed using the VASP software package. The results of calculations of stiffness tensors, Young's modulus, and Poisson's ratios show that all studied single-element 2D materials are mechanically stable. Dynamic stability was investigated by calculating the phonon dispersion of the materials using the finite displacement method. Only Pb_2 has imaginary modes in the phonon dispersion curves and therefore it has dynamic unstable structure at low temperatures. The analysis of the band structures indicates the presence of insulators (N_2), semiconductors (P_2, As_2, Bi_2, Sb_2), semimetals, and metals among the studied group of single-element 2D materials.

Keywords: 2D material, ab initio, elastic constants, phonon dispersion, band structure.

Conflict of interests. The author declares no conflict of interests.

Gratitude. This work was supported by the grant 3.02.3 of Belarusian National Scientific Research Program "Convergence-2025" and the grant of The Belarusian Republican Foundation for Fundamental Research for young scientists "Science M - 2021" (contract № F21M-122). Computing cluster of BSUIR was used for computer modeling.

For citation. Hvazdouski D.C. First-principles study of stability and electronic properties of single-element 2D materials. Doklady BGUIR. 2021; 19(8): 92-98.

Introduction

Atomically thin two-dimensional (2D) materials have made their way to the forefront of several research areas including batteries, electrocatalysis, electronics, and photonics [1]. This development has been prompted by easily tunable properties of atomically thin crystals. Recently, the concepts of horizontal [2] and vertical [3] 2D heterostructures have appeared, it provides new possibilities to create materials with special electrophysical properties.

So far more than fifty compounds have been synthesized or exfoliated as single layers. These include the well-known single-elemental crystals and their ligand functionalized derivatives, transition metal dichalcogenides, transition metal carbides and -nitrides, group III–V semiconductors and insulators, transition metal halides, post-transition metal chalcogenides, and organic-inorganic hybrid perovskites.

A common feature of 2D materials is that they are formed from bulk materials with strong in-plane interatomic bonds and weak van der Waals (vdW) interaction between layers. It allows them to delaminate into atomically thin layers that can be investigated separately.

An important task is to determine the stability of two-dimensional materials using a numerical experiment, in particular, using the *ab initio* methods, it is much cheaper than a physical one. There is a possibility to simulate conditions that cannot be created in the laboratory in the course of a numerical experiment. Therefore, the material over a wide range of characteristics can be investigated. Synthesized materials must simultaneously satisfy thermodynamic, mechanical, dynamic, and thermal stability.

First-principles calculations are playing an increasingly important role in the search for new materials with required properties and functionalities. First-principles calculations are comparable with the experiments in terms of accuracy and greatly surpass them in terms of speed and cost through the continuous increase of computing power and significant advancements of theoretical methods and numerical algorithms. Structural, thermal, and electronic properties of 2D materials have been an insufficiently explored area of material science and, in the last decade, the experimental data has been augmented by an explosion of the computational data obtained from first-principles calculations. Density functional theory (DFT) methods are quite reliable for ground state properties such as structural and thermodynamic properties. They are generally not quantitatively accurate for excited state properties such as electronic band structures and optical absorption spectra.

In this work we performed a series of *ab initio* calculations to investigate the stability and electronic properties of single-elemental 2D materials previously unknown and potentially synthesizable monolayers.

Methods of calculation

Calculations of the total energy and electronic structure of the materials under study were performed using the VASP software package [4]. The electron-ion interaction was described using the projection augmented wave (PAW) method, and exchange correlation energy (XC) was taken into account using the GGA functional in the form of a PBE potential [5]. For the basis of plane waves, a cutoff energy of 450 eV was taken. To avoid the influence of wave functions on each other, arising from the translation of cells in a plane model of 2D systems, periodic plates of single-element 2D materials were separated by a 15 Å-thick vacuum layer along the crystallographic direction "*c*". The nonbonding van der Waals (vdW) interaction between atoms is taken into account using the semiempirical Green's dispersion correction scheme with Becke and Johnson's corrections [6] named "DFT-D3(BJ)". It is known that the studied monolayers of Si, Ge, and Sn don't possess spin polarization (they are nonmagnetic materials) and further calculations were performed without taking into account the spin polarization. The Bloch vectors of the first Brillouin zone were carried out using the *k*-point sampling. Self-consistent calculations were carried out with *k*-point grids generated automatically by the Monkhorst–Pack scheme with inverse spatial resolution of $2\pi \cdot 0.03$ Å^{-1}. Structural relaxation of the geometry and structural parameters of the primary unit cells were carried out until the residual force per atom became less than 0.001 eV/Å.

For a two-dimensional crystal, the stiffness tensor in the plane C_{ij} (i, j = 1, 2, 6) can be obtained by the following formula:

$$E_s = \frac{1}{2}C_{11}\varepsilon_{xx}^2 + \frac{1}{2}C_{22}\varepsilon_{yy}^2 + C_{12}\varepsilon_{xx}\varepsilon_{yy} + 2C_{66}\varepsilon_{xy}^2, \quad (1)$$

where ε is the tensile/compressive strain, which is defined as:

$$\varepsilon = \frac{a - a_0}{a}, \quad (2)$$

where a and a_0 are the lattice constants of the deformed and undeformed crystal, respectively.

To calculate the elasticity constants, the $E_s(\varepsilon)$ function was investigated in the deformation range of $-1.5\ \% \le \varepsilon \le 1.5\ \%$ with a step of 0.5 %. The elasticity constants C_{ij} were obtained by fitting a second-order polynomial of the total energy change function of the system depending on the applied deformation. Post-processing of the calculated data was carried out the VASPKIT code [7].

Dynamical stability of the 2D materials has been defined by phonon dispersion which is evaluated by the finite displacement method realized in the Phonopy program [8]. We have utilized a 5×5×1 supercell for 2D structures and the atomic displacement distance of 0.01 Å. Force constants

based on the forces on atoms were calculated using the POSCAR-{number} files to VASP calculations. Then a part of dynamical matrix was built in the Phonopy program from the force constants. Phonon frequencies and eigenvectors are calculated from the dynamical matrices with the specified *q*-points.

Structure optimization of single-elemental 2D materials

Configurations of potential single-element two-dimensional materials based on 10 chemical elements were proposed. For each of the chemical elements, 5 configurations with a hexagonal type of crystal lattice were proposed (Fig. 1).

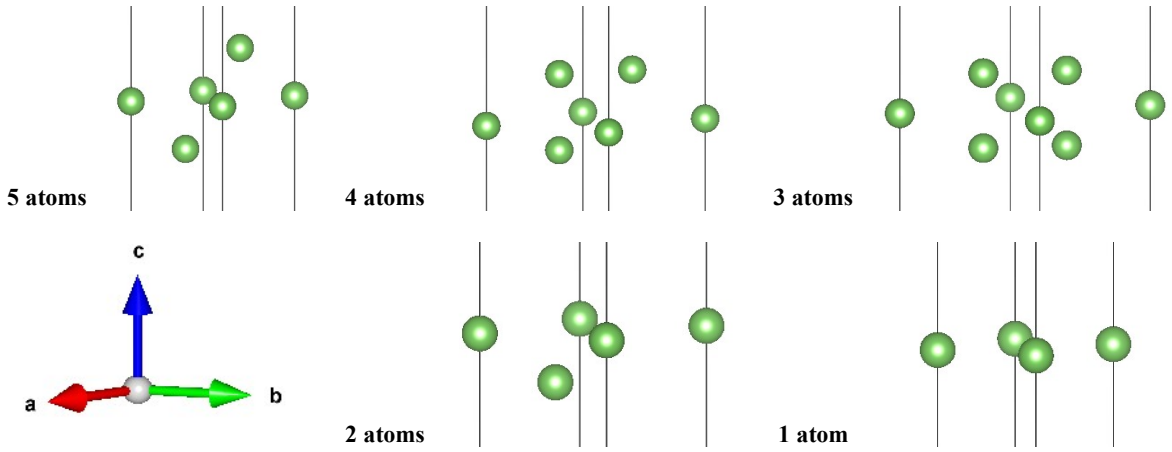

Fig. 1. Configurations of potential single-element 2D materials with a hexagonal lattice type

Structural optimization of the these configurations has been carried out. Based on the obtained values of the total energies of the systems (Tab. 1), it was concluded that configurations of two atoms are energetically favorable for the 2D systems under study. Thus, further calculations of stability and electronic properties were carried out for 2D systems with unit cells of two atoms.

Table 1. Values of total energies of systems for different single-element 2D material configurations

Atoms in a cell	Total energy of cell, eV/atom									
	As	Bi	C	Ge	N	P	Pb	Sb	Si	Sn
1	–4.05	–3.49	–5.33	–3.87	–4.24	–3.85	–3.19	–3.65	–3.98	–3.42
2	–4.87	–4.01	–9.31	–4.59	–6.76	–5.57	–3.66	–4.28	–4.97	–3.88
3	–4.54	–3.91	–6.32	–4.20	–5.11	–5.26	–1.15	–4.11	–4.87	–3.71
4	–4.45	–3.60	–9.11	–4.32	–4.77	–5.07	–3.13	–4.02	–4.56	–3.76
5	–4.58	–3.94	–8.22	–4.28	–4.72	–5.01	–3.39	–4.13	–4.77	–3.64

The calculated total energies E_{tot} and lattice constants "*a*" of all studied 2D systems after structural relaxation are listed in Tab. 2.

Table 2. Structural properties of single-element 2D materials

Parameter		Single-element 2D material									
		C_2	N_2	Si_2	P_2	Ge_2	As_2	Sn_2	Sb_2	Pb_2	Bi_2
a, Å	LDA	2.45	2.29	3.83	3.21	3.96	3.53	4.56	4.02	3.55	4.29
	PBE	2.46	2.29	3.86	3.25	4.02	3.59	4.65	4.08	3.62	4.36
	Ref. [9]	2.46	–	3.88	–	4.02	–	4.66	–	–	–
E_{tot}, eV	LDA	–20.18	–13.37	–10.41	–11.84	–9.16	–10.46	–7.79	–9.13	–7.93	–8.58
	PBE	–18.63	–13.52	–9.95	–11.15	–8.39	–9.74	–7.13	–8.57	–7.23	–7.99

The presented results of calculations with a PBE exchange correlation functional are in good agreement with previous theoretical investigations. The calculated value of lattice constant "*a*" has PBE only 0.8 % smaller than the theoretical value, which points it out as a good approach of an exchange

correlation energy functional in order to calculate the lattice parameters. The observed discrepancy of LDA and PBE of our results compared to the experimental values is a well-established fact.

Stability of single-elemental 2D materials

Dynamic stability reflects the ability of a material to maintain its shape under mechanical perturbations of the structure, which can be determined by calculating the phonon spectrum of the material using the finite displacement method [10] or the density functional perturbation theory. If imaginary modes exist in the phonon spectra, this means that the material, after a slight distortion of the crystal lattice, will undergo reconstructive or martensitic phase transformations. Thermal stability reflects the resistance to the degradation at high temperatures, which can be estimated by performing *ab initio* simulations using molecular dynamics methods. The thermodynamic stability of two-dimensional materials is characterized by the formation energy ΔE_f. It is defined as the difference between the energies of the investigated 2D material and its pure elementary components. A negative value of ΔE_f for a material indicates its thermodynamic stability. In other words, any processes that lead to transformation or decomposition of the material are unacceptable or kinetically slow. In this study, only dynamic and mechanical stability were used as two stability criteria for the selection of potential 2D materials. Thus, if a 2D material is found to be stable and has a band gap unlike zero eV, this means, that it may be a new potential two-dimensional semiconductor.

In this work, only the phonon dispersion and elastic constants of two-dimensional materials were calculated. In this case, it is possible to achieve a better ratio between the expenditure of computer time and the deviation of the simulation results from the experimental data.

According to the Born – Huang criteria [11], a mechanically stable 2D sheet must match the requirements of $C_{11} > 0$ and $C_{11} > |C_{12}|$. Then Young's modulus Y and Poisson's ratios ν for a two-dimensional material can be defined as:

$$Y(x) = \frac{C_{11}C_{22} - C_{12}^2}{C_{22}}, \quad Y(y) = \frac{C_{11}C_{22} - C_{12}^2}{C_{11}}, \tag{3}$$

$$\nu(x) = \frac{C_{12}}{C_{22}}, \quad \nu(y) = \frac{C_{12}}{C_{11}}. \tag{4}$$

where x and y correspond to the lattice directions a and b, respectively.

The mechanical properties of single-element 2D materials calculated using *ab initio* methods and presented in Tab. 3. Authors [9] calculated the planar elastic stiffness coefficients C_{11}, C_{22}, and C_{12} using a central difference approximation to the derivative of the stress tensor for the studied materials. The calculated Young's modulus is in good agreement with the previous theoretical calculations for silicene (61.33 N/m), germanene (42.05 N/m), and stanene (24.46 N/m) [12]. According to the Born–Huang criteria, it was found that all studied single-element 2D materials are mechanically stable.

Table 3. Mechanical properties of single-element 2D materials

Parameter		Single-element 2D material									
		C_2	N_2	Si_2	Ge_2	Sn_2	Pb_2	P_2	As_2	Sb_2	Bi_2
This work	C_{11}, N/m	343.07	269.68	69.28	49.78	27.04	15.62	77.73	52.91	32.89	25.04
	C_{12}, N/m	78.82	27.31	22.19	17.69	10.99	5.65	8.73	9.57	5.74	6.27
	ν	0.23	0.11	0.32	0.35	0.41	0.36	0.11	0.18	0.17	0.25
	Y, N/m	324.96	266.92	62.17	43.49	22.57	13.58	76.75	51.16	31.89	23.47
Ref. [9]	C_{11}, N/m	345.65	–	66.62	48.87	28.56	–	77.37	52.51	32.61	24.49
	C_{12}, N/m	70.61	–	21.51	16.22	11.41	–	7.95	8.50	6.23	6.05

A crystal will be dynamically stable, if its potential energy always increases against any combinations of atomic displacements (all phonons have real and positive frequencies). However under virtual thermodynamic conditions, imaginary frequency or negative eigenvalue can appear. This indicates dynamical instability of the 2D crystal phase. The calculated phonon dispersions of single-element 2D materials are shown in Fig. 2.

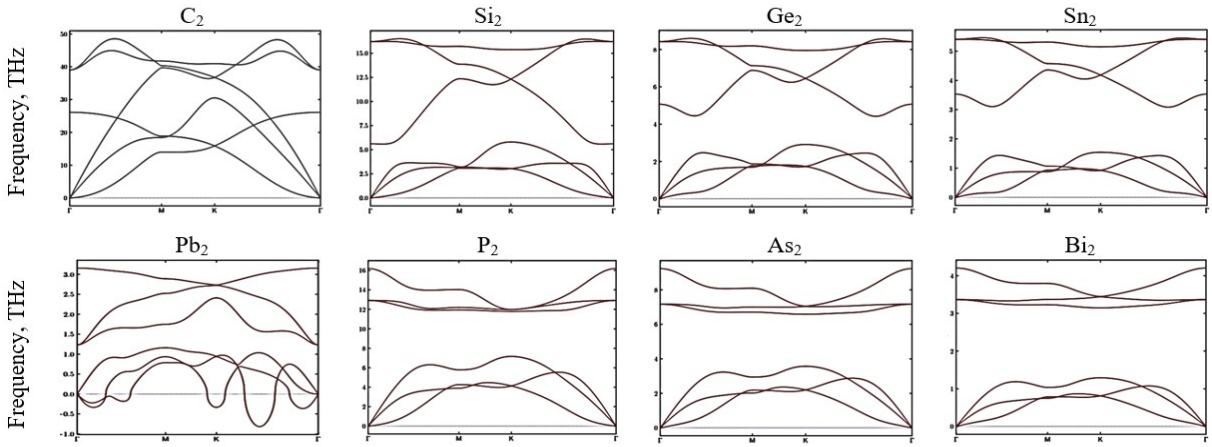

Fig. 2. Phonon dispersions of single-element 2D materials

Almost all single-element 2D materials do not have imaginary frequencies in the phonon dispersion curves and they can be viewed as dynamically stable structures. However, Pb_2 has imaginary frequencies (negative values) in the vicinity of the Γ, M, and K points indicating instability against phonon excitation. This indicates that Pb_2 is unstable at low temperatures. The imaginary frequencies can arise from the numerical inaccuracy because of the limited supercell size.

For a more accurate analysis of the stability of materials, it is planned to carry out a number of calculations based on the theory of perturbations of the density functional and molecular dynamics to determine the thermal stability of two-dimensional materials.

Electronic properties of single-elemental 2D materials

Electronic band structures are calculated along the high symmetry paths of 2D Bravais lattices. The band energies are computed within DFT method using three different XC-functionals: LDA, PBE, and HSE06. The electron density is determined self-consistency on a uniform *k*-point grid of density 10.0/ $Å^{-1}$. From this density, the PBE band structure is computed non-selfconsistency at 200 *k*-points distributed along the band path. The band structure is calculated non-selfconsistently using the range-separated hybrid functional HSE06 on top of a PBE calculation with *k*-point density 12.0/ $Å^{-1}$ and 600 eV plane wave cutoff.

Tab. 3 shows the results of calculating the electronic properties of single-element 2D materials using LDA, PBE, and HSE06 XC-functionals.

Table 3. Electronic properties of single-element 2D materials

Single-element 2D material	Band gap, eV			Band Character	Location of valence band maximum			Location of conduction band minimum		
	LDA	PBE-D3(BJ)	HSE06-D3(BJ)							
C_2	0.000	0.000	0.000	Semimetallic	0.333	0.333	0.000	0.333	0.333	0.000
N_2	3.845	3.878	5.809	Indirect gap	0.144	0.144	0.000	0.329	0.000	0.000
Si_2	0.000	0.000	0.000	Semimetallic	0.333	0.333	0.000	0.333	0.333	0.000
P_2	1.863	1.987	2.753	Indirect gap	0.000	0.000	0.000	0.362	0.000	0.000
Ge_2	0.000	0.000	0.000	Semimetallic	0.333	0.333	0.000	0.333	0.333	0.000
As_2	1.455	1.564	2.189	Indirect gap	0.000	0.000	0.000	0.313	0.000	0.000
Sn_2	0.000	0.000	0.000	Semimetallic	0.333	0.333	0.000	0.333	0.333	0.000
Sb_2	1.113	1.485	1.183	Indirect gap	0.000	0.000	0.000	0.310	0.000	0.000
Pb_2	–	–	–	Metallic	–	–	–	–	–	–
Bi_2	0.566	0.568	0.977	Direct gap	0.000	0.000	0.000	0.000	0.000	0.000

The band gap and the type of semiconductor were indicated for the studied compounds. The band gap of semiconductors is greatly underestimated when calculating the traditional density functional theory (DFT) with local or semilocal exchange correlation functionals. The results obtained may differ from the experimental values ones in the direction of underestimating the band gap due to the well-known difficulties arising in the framework of the DFT.

The calculated band structures of single-element 2D materials (As_2, C_2, Bi_2, N_2) with LDA, PBE, and HSE06 XC-functionals are presented in Fig. 3.

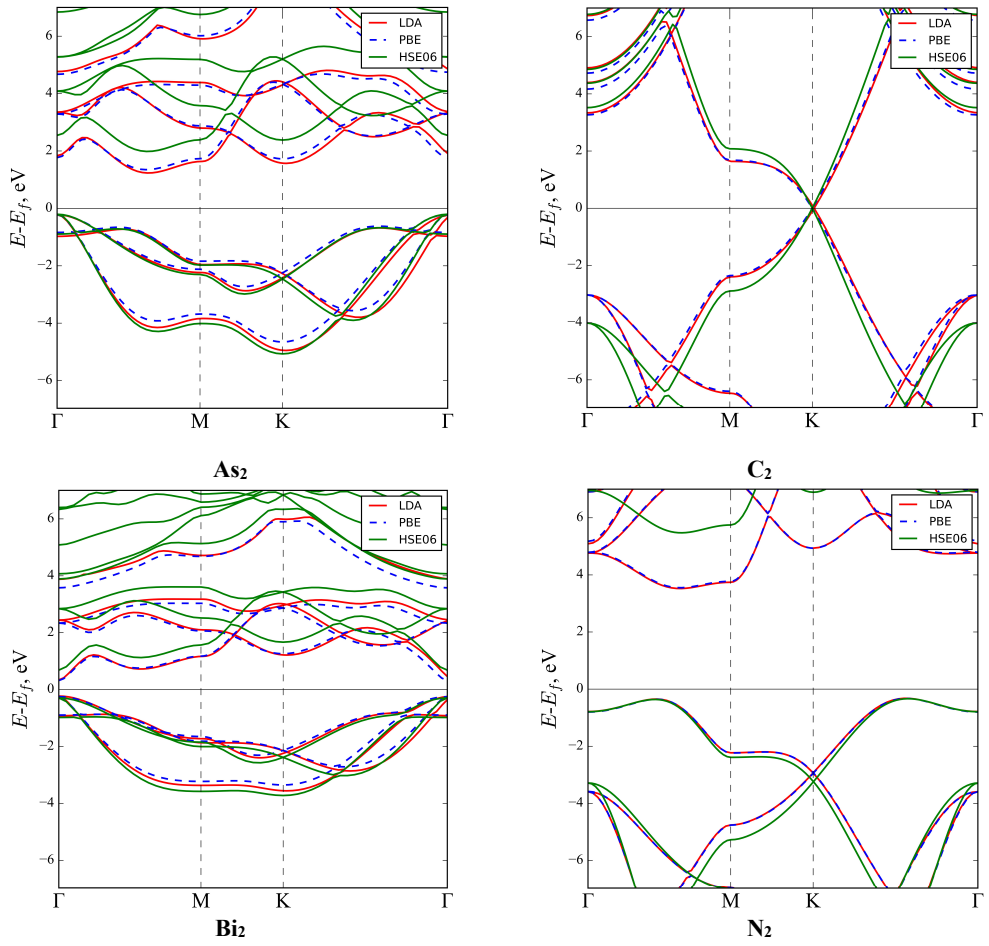

Fig. 3. Electronic band structures of single-element 2D materials

The band structures of the studied single-element 2D materials were obtained and according to which the type of conductivity was established. It was found that N_2 is indirect-gap insulator with a band gap of 5.809 eV. P_2, As_2, and Sb_2 are indirect-gap semiconductors with bandgaps of 2.753, 2.189, and 1.183 eV, respectively. Bi_2 is a direct-gap semiconductor with a band gap of 0.977 eV. C_2, Si_2, Ge_2, and Sn_2 are semimetals with direct transitions. Pb_2 is a 2D metal-type material (the Fermi level in this case crosses the conduction bands).

Conclusion

The results of *ab initio* calculations of mechanical properties in the present study are in good agreement with the previous theoretical calculations. It shows that all studied single-element 2D materials are mechanically stable. The calculated phonon properties of almost all 2D materials (except Pb_2) don't have imaginary frequencies in the phonon dispersion curves and they can be viewed as dynamically stable structures. Pb_2 is unstable at low temperatures. It is necessary to carry out additional calculations based on the molecular dynamics for a more accurate analysis of the stability of materials.

The analysis of band structures indicates the presence of insulators (N_2), semiconductors (P_2, As_2, Bi_2, Sb_2), semimetals, and metals among the studied group of single-element 2D materials. The results obtained quantitatively and qualitatively characterize the structural and electronic properties of crystal structures based on 2D materials. The results can be used in the development of methods for calculating the basic electrophysical parameters of promising devices for nanoelectronics and optoelectronics.

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