

PEOPLE'S DEMOCRATIC REPUBLIC OF ALGERIA
Ministry of Higher Education and Scientific Research
University of Amar Telidji - Laghouat



Faculty of Technology
Department of Electronics

Ph.D. Thesis in **Electrical Engineering**
Major: **Photovoltaics Physics**

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**Silicon-based Clathrates: Potential materials for
energy conversion applications.**

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2017-2018

ACKNOWLEDGMENTS

*I would like first to express my deep gratitude and appreciation to my doctoral supervisor **Pr. Marhoun Ferhat** for giving me such a great scientific journey, for providing patient guidance, encouragement and support along the six years of this degree. He, by his skills and talent, has inspired me to accomplish the goals of this thesis. His lessons and advice will benefit me for a lifetime. Thank you very much Sensei.*

*Many thanks to **Dr. Toyohiro Chikyow** of the National institute for materials science **NIMS in Japan**, for inviting me without any to accomplish many visits to his lab and for giving me a chance to work with world-class scientist within cutting-edge facilities. My deep appreciation to the NIMS scientists and staff I met there, and who were, certainly, a part of this journey.*

*My gratitude goes also to **Pr. Mohamed BOURENNANE**, for his warm welcome and generosity during my visits to his laboratory at the Albanova research center, University of Stockholm, **Sweden**.*

*I express my sincere thanks to **Pr. Ibn Khaldoun LEFKAIER**, Professor at the University Amar Têlidji of Laghouat, for having accepted to chair the Jury of this dissertation.*

*My sincere appreciation to **Dr. Rachid BELKADA**, research director at CRTSE (Centre de Recherche en Technologie des semi-conducteurs pour l'énergétique, Algiers) for his fruitful collaborations and contributions to our papers and conferences.*

*I would also like to say a big thank you to the members of the jury: **Pr. Khelil Bouamama** Professor at the University Ferhat Abbas of Sétif , **Dr. Bachir HELIFA** Lecturer at the University Amar Têlidji of Laghouat, and **Dr. Abdelhak CHETTAH** Lecturer at the University of Sekikda, who have Accepted, without any reserve, to evaluate this thesis to its true value, and to share with me their remarks surely relevant, which, with a little hindsight, will undoubtedly contribute to the improvement of this work. THANKS!*

N. A. Mahammedi

Dedications

This work is dedicated to those who have given me the strength and the courage along this journey...

To My great parents Dr. Lamine and Hassiba, who never stopped giving of themselves in countless ways...

To my dearest wife Asma, who led me and still through the hills of life with light of hope and support, and to her dear family...

To my beloved brother Adel and sister S. Feriel who stood by me when things looked bleak, who wholly sweetened up my life

To my beloved nephews: Anis and Dalia, and their father Adel, whom I can't force myself to stop loving....

To all my family, the symbol of love and giving

To my friends from all over the world, who enriched my life through the warmth of friendship and compassion, who encouraged and supported me through this journey....

All the people in my life who touched my heart, I dedicate this research.....

Nassim Ahmed Mahammedi

PREFACE

This article-based thesis is the fruit of my doctoral journey which includes the most important work I undertook along. The main two articles are fully included as chapters after approval of the journals to the authors.

Full content of Chapter IV of this thesis was published as SUPERLATTICES AND MICROSTRUCTURES journal, *Volume 100, December 2016, Pages 296-305(copyright Scopus 2016)*. Content of Chapter V was published at the JOURNAL OF APPLIED PHYSICS, *Volume 122, 205103 (2017), November 2017(copyright American institute of physics AIP 2017)*. The author of

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N. A. Mahammedi

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CHAPTER I

General Review of Group-IV Inorganic Clathrates

Abstract

This chapter presents a detailed description and fundamental structural aspects of clathrate materials. In the first part a general overview including etymological and historical reviews on clathrates are given, followed by a description of different forms of silicon clathrates and how they are distinguished. Particular attention and more details are given for the type-I and type-VIII, which are the main subjects of this thesis study. Finally, the importance of the ‘guest atoms’ and their influence is discussed.

I.1. Introduction: What are clathrates?

The term ‘Clathrate’, which means ‘inclusion’ or ‘cage-like material’, is derived from the Greek word ‘Klethra’ originally meaning ‘alder’ [1]. It was first used by Powel in 1948 in his works on organic inclusion compounds as β -quinol [2]. That term was extended to describe solid gas hydrates in 1952 by Pauling and Marsh [3], (Linus Pauling was awarded the Nobel prize of chemistry in 1954 for his works). Since then, the term clathrate was adopted to describe any material whose main lattice is formed by cage-like framework that encloses guest atom or molecule within. Figure.I.1 illustrates a hydrate clathrate where the framework is formed by H_2O molecules arranged in a way to form a cage-like structure, and CH_4 methane molecules are entrapped inside the framework [4]. The main characteristics of clathrate compounds are:

- (1) The unit-cell is usually large, highly symmetrical and the lattice constants almost independent of the nature of the guest species, which can be an atom or a molecule.
- (2) The host lattice itself can be considered as a possible allotropic form of the major species, which is stabilized by the presence of guest species.
- (3) The guest lattice can be non-stoichiometric and even guest-free clathrates exist.
- (4) At high temperature, they decompose into the starting chemical species, and correspond to a kind of association rather than a combination.

(5) The host-guest interactions affect the properties of clathrates. They are generally weak as in clathrate hydrates, but they can be stronger as in inorganic clathrates. Several families of clathrates are known, the host lattice of which are of inorganic or organic nature.

The most important and representative of them is the series of the so-called gas and liquid hydrates, in which the host lattice is made of corner sharing H_2O tetrahedrons forming large cages of 20 to 36 vertices, in which are enclosed guest molecules of a gas (Cl_2 , SO_2 , CH_4 , H_2S , Kr, etc.), or a liquid (C_6H_6 , CH_3I , CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4 , etc.).

I.2. A little history of inorganic clathrates

In 1811 H. Davy reported the first evidence of a compound of water cage-like structure containing chlorine gas molecules, the compound will be later known as a **hydrate clathrate** [5]. In 1823 Michael Faraday successfully determined a composition for this compound and reported it as $(\text{Cl}_2)_1(\text{H}_2\text{O})_{10}$ [6]. It was only after the introduction of x-ray diffraction, and more than a century later (1951), that the crystalline structure of this compound was determined. Claussen [7] and Pauling & Marsh [3] independently determined that hydrate clathrate of chlorine was in fact built of a hydrogen-bonded network of water, with the oxygen atoms forming cage-like networks within which chlorine atoms are confined as "guests". The correct stoichiometry was determined as $(\text{Cl}_2)_1(\text{H}_2\text{O})_8$.

Today, several hydrate clathrates structures are known, and a variety of guest gas and solvent atoms are known to be trapped in the cages formed by water. The Merriam-Webster™ dictionary defines the word "clathrate" (pronounced *klathrat*) as "relating to or being a compound formed by the inclusion of molecules of one kind in the cavities of the crystal lattice of another" [8]. The etymology of the word clathrate can be traced to Latin roots *clathratus* for "furnished with a lattice", *clathri* (plural) for "lattice"; and the Greek roots *kleithron* for "bar" and *kleiein* for "to close" [8]. Today, the word clathrate is used to describe compounds which display a host-guest relationship.

In 1965, it was observed that the x-ray diffraction patterns resulting from the thermal degradation of certain silicides were similar to those of ice clathrates: an observation that led to the discovery of a new class of clathrates formed of tetrahedrally bound silicon [9].

Inspired from hydrate clathrates, Group-IV clathrates, and precisely silicon-based clathrates are the most studied and promising clathrates as they exhibit a variety of possible technological interest as well as the wide range of possible introduction of many atomic species, thus, type-II clathrates with the chemical formula $\text{Na}_x\text{Si}_{136}$, were the first silicon clathrates to be synthesized in

1965 by two French groups, i.e. Cros et al [10] and Kasper et al [11]. This class of materials encountered small amount of interest until the mid-1990s were exceptional superconducting and semiconducting properties were discovered [12].

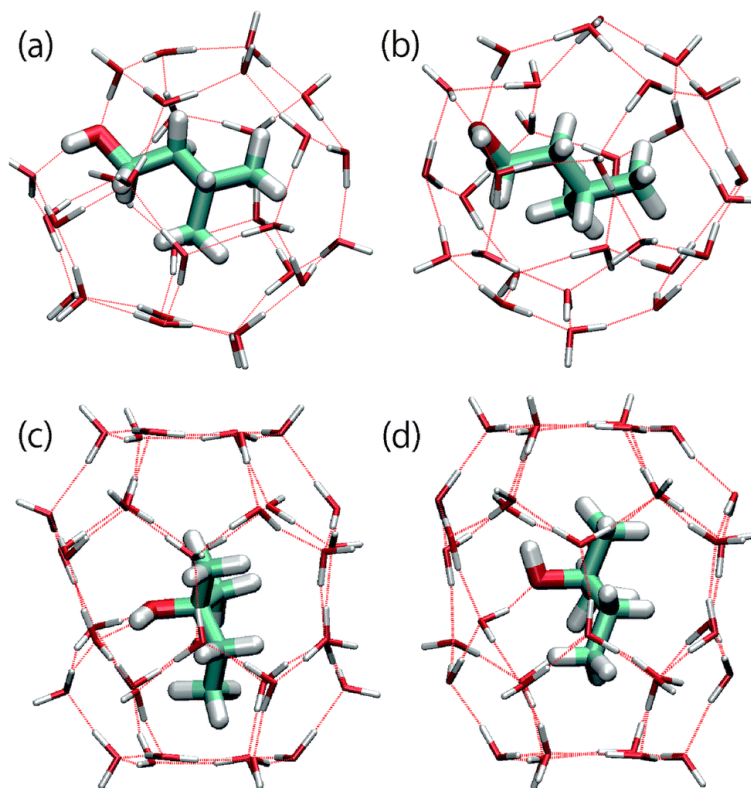


Figure.I.1. Snapshots of the $5^{12}6^4$ cages in sII and $5^{12}6^8$ cages in sH clathrate hydrates from the *ab-initio* MD simulations. The O–H group of 3-methyl-1-butanol molecules in sII hydrates is incorporated into $5^{12}6^4$ cages and forms hydrogen bonds with (a) two or (b) three water molecules. The O–H group of 2-methyl-2-butanol molecules in sH hydrates forms hydrogen bonds with (c) two or (d) one water molecules.

Silicon, germanium, tin and carbon are often discussed in comparison with each other in terms of the same group-IV elements. Since the discovery of carbon cluster C_{60} (fullerene), it has been expected that similar type of clusters should be prepared with silicon, germanium or tin. As a matter of fact, there are silicon clathrate compounds which are composed of silicon polyhedra analogous to fullerenes. Silicon clathrate compounds, M_xSi_{46} and M_xSi_{136} ($M = Na, Ba, K, Ca, Rb, Cs$) were first prepared and extensively studied by Kasper *et al* [9]. The compounds are composed of Si- sp^3 bonds with about the same bond distances and bond angles as in elemental diamond silicon, but the silicon tetrahedra build an open network having pentagonal dodecahedra (12 pentagonal faces, $[5^{12}]$), and tetrakaidecahedra (12 pentagonal faces and 2 hexagonal faces, $[5^2 6^2]$), for M_xSi_{46} , and pentagonal dodecahedra ($[5^{12}]$) and hexakaidecahedra (12 pentagonal faces and 4 hexagonal faces, $[5^{12} 6^4]$) for type-II clathrate M_xSi_{136} . These polyhedra are connected three dimensionally by

face sharing, alkali metal atoms (M) being placed at the center of the polyhedra. The crystal structure of two cubic clathrate types were described, one containing 46 silicon atoms (type-I), and the other containing 136 silicon atoms (type-II) in the unit cell. The arrangement of the silicon atoms results in the formation of cage-like motifs as in the hydrate clathrates, and sodium was intercalated as guest atom. Within few years of this discovery, the synthesis and structure of the germanium and tin analogs were also described [9]. It is interesting to note similarities between the silicon clathrate compounds and alkali-metal doped fullerenes; both structures consist of polyhedra of group-IV elements containing alkali-metals in the structure, although there is a significant difference between the two solids; the Si is sp^3 whereas C is sp^2 in the fullerenes, and the clusters of fullerenes are not bonded to each other, in contrast to the silicon clathrate compounds with covalent bonding [13]. The metal atoms in the silicon clathrate compounds are doped within the silicon cages rather than outside as in the case of fullerene doping. The clathrate compounds are stable in air even in acid solutions except hydrofluoric acid. Since the discovery of superconductivity in alkali-metal doped fullerenes [14], much attention has been paid to silicon clathrate compounds because of the possibility of having new superconductors [12]. S. Yamanaka *et al* have succeeded in preparing barium-containing silicon clathrate Ba_8Si_{46} compounds isomorphous with the NaSi type structure [15], and found that the compound became the type II superconductor with a critical temperature of about 4 K. The compound was prepared through the high pressure high temperature HPHT technique from a ternary Zintl-phase of barium silicide.

The structurally related carbon-based fullerenes [16], which contain five- and six-membered rings of sp^2 connected carbon atoms (in contrast, the Si atoms are sp^3 bound in the clathrates) are known to become metallic and superconducting upon interstitial doping with alkali metals [8]. Motivated by this discovery of high T_c compositions in the alkali metal- C_{60} systems, Roy *et al* [17] [17] re-examined the electrical and magnetic behavior of Na_xSi_{136} down to 2 K. However, their report led Yamanaka *et al.* to the composition $Na_xBa_ySi_{46}$ which was found to become superconducting at 4 K [15]. Subsequently, phases of the formula $Ba_8M_xSi_{46-x}$ ($M = Au, Ag, Cu$) were shown to have superconducting critical temperatures in the range 5-6 K [18], and more recently, Ba_8Si_{46} was observed to superconduct at 8K the highest reported for any sp^3 bonded structure at ambient pressure [15]. The pioneering theoretical study [19] on the energetics and electronic structure of Si_{46} and Si_{136} led to two important conclusions: **(i)** that the bandgap of these materials is about 0.7 eV larger than that of elemental silicon and **(ii)** that Si_{46} and Si_{136} are significantly lower in energy than dense high-pressure polymorphs of silicon, and only a few meV

higher than the stable diamond structure. This result suggested that guest-free Si_{46} and Si_{136} could be technologically important opto-electronic materials if experimentally realized. The host-guest nature of the clathrates results in some unique mechanisms for electron and thermal transport. It has been suggested that electrical conduction occurs primarily via the framework atoms, the guest atoms playing only a passive role. Thermal conduction also occurs via framework atoms in the form of lattice vibrations, however, the translational motion of the guest atoms interfere with the framework vibrations, resulting in anomalous glassy behavior of certain compositions, while not affecting electron transport [20-22]. The structural elegance of silicon and germanium clathrates initiated the original works, however, it has only been the last decade that has witnessed a renewal of interest in these materials testified by the large number of articles reporting on the unique physical, chemical and structural properties of these materials.

I.3. Structures of some silicon clathrates

According to their composition, structures, the nature of their constituent cages and the way they associate, several types of inorganic clathrates can be distinguished. Theoretically, ten types of silicon clathrates can be classified, but only four types are realized experimentally, i.e. type-I, type-II, type-III and type-VIII. The type-I clathrate with the formula X_8Si_{46} , (X=guest atom), is the most investigated clathrate, and to the date about 122 compound are known through the partial or complete substitutions of host or guest atoms. Type-II clathrates having a chemical formula of $\text{X}_6\text{Si}_{136}$ were also synthesized as bulks and successfully grown as thin films among all clathrates, additionally, a thin film of Si_{136} was grown over Si (100) substrate and has shown a direct bandgap but no optical activity was recorded. In this section a general view over the existing and hypothetical structures of clathrates is detailed and discussed.

I.3.1. Type-I clathrate

Type-I clathrate is the first known form of all clathrates, it was first synthesized in 1965 in its inorganic group 14 [9]. With formula X_8Si_{46} , while its hydrate counterpart analog was known, it was only reported in 1965 as mentioned above. Type-I clathrates crystallize in the Pm-3n space group (number 223), which presents a simple cubic unit cell. The main lattice of type-I clathrate structure is formed from association of dodecahedrons (twelve pentagonal faces with 20 atoms on edges [5¹²]) with tetrakaidecahedrons [23]. Tetrakaidecahedra polyhedron are connected to each other by

sharing their hexagonal faces and with other dodecahedrons by sharing their pentagonal faces, while dodecahedrons are connected to each other by sharing their

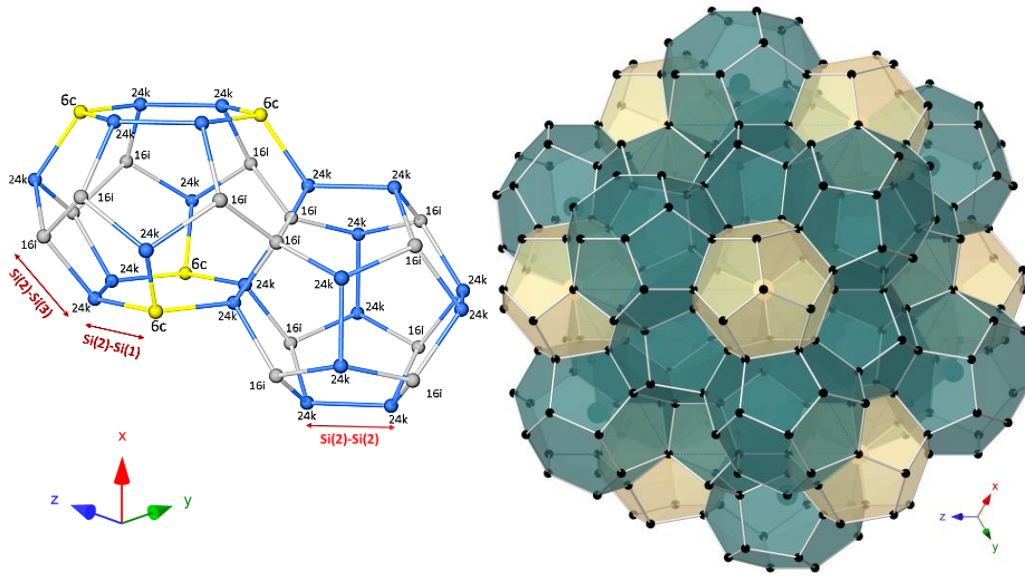


Figure.I.2 Type-I Si clathrate is composed from the association of dodecahedral and tetrakaidecahedral cages [24].

I.3.2. Type-II clathrate

Type-II clathrates are initially composed from thorough associations of eight large hexakaidecahedra (28-vertex with 16 faces [$5^{12}6^4$]) together with sixteen pentagonal dodecahedra [5^{12}]. Type-II clathrates usually crystallize in the face-centered cubic FCC space group Fd3m. The hexakaidecahedra share all of their hexagonal faces forming a diamond-like 3D network (Figure I.3). Additionally, each hexakaidecahedron is encircled by twelve pentagonal dodecahedra, forming a truncated tetrahedron. Thus, the space is fully filled. The unit cell of type-II clathrate contains 16 small and 8 large polyhedra, with a generalized formula of X_6M_{24} or $X_{24}M_{136}$ (X is the guest atom and M is the group-IV host atom, Silicon in our case). Both cages can be filled with the same type of guest atoms, like Na, or with two different types of guests, like Na and Cs, with the larger cation occupying the larger cages [25]. So far, anionic type-II clathrate structures with frameworks based on Si, Ge, and Sn atoms have been reported [26, 27]. The relative ratio of the framework cage volumes to the guest cation radii determines which type of cages host the vacancies [28]. In the Na_xSi_{136} clathrates for example, for compositions with sodium content x less than 3, Na atoms tend to occupy the large hexakaidecahedral cages [$5^{12}6^4$] [29]. In contrary for Sn-based clathrate-II structures with Ba and K guests, only pentagonal dodecahedral cages [5^{12}] are occupied, and the

hexakaidecahedra are not [30]. It is not uncommon for type-II clathrate structures to be partially filled, or even completely empty “guest-free” [31]. The guest-free type-II germanium clathrate Ge_{136} was described as new allotropic structure of germanium, and it was prepared by a mild oxidation of Na_4Ge_9 in ionic liquids [31]. Additionally, an empty silicon-based clathrate-II with an extremely small residual Na content was prepared by annealing $\text{Na}_x\text{Si}_{136}$ with iodine [32]. And a thin film of guest free type-II silicon clathrate was for the first time successfully grown over a Si(111) substrate by means of vapor deposition and subsequent heat treatment within iodine [33].

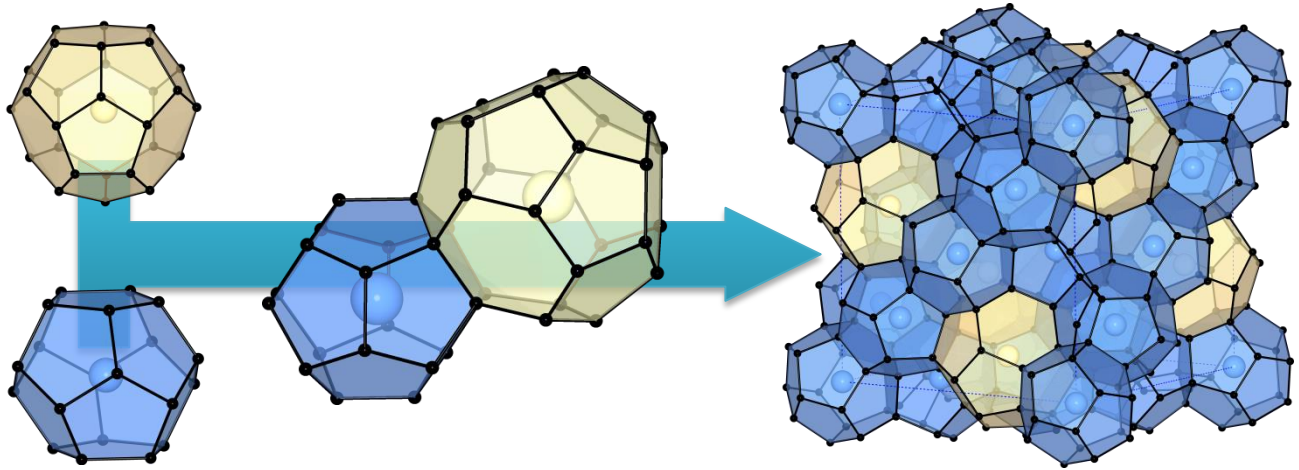


Figure I.3: Type-II silicon clathrate $\text{X}_{48}\text{Si}_{136}$

I.3.3. Type-III clathrate

The crystalline structure of type-III clathrate is composed from three types of polyhedra, i.e. ten dodecahedra $[5^{12}]$, sixteen tetrakaidecahedra $[5^{12}6^2]$, and four pentakaidecahedra $[5^{12}6^3]$. It crystallizes in the tetragonal space group $\text{P}42/\text{mnm}$. The tetrakaidecahedral cages form a sort of two distinct columns running along the $\langle 001 \rangle$ crystallographic direction (Figure III.4). The first type of column is made by the sharing of hexagonal faces. Whereas, the second type of column is made of the tetrakaidecahedra. After association of polyhedra, the remaining space will be filled by isolated pairs of either the pentakaidecahedra $[5^{12}6^3]$ or the $[5^{12}]$ dodecahedra. There are 172 host framework atoms in these clathrates, and their formulas can be generalized as $\text{X}_{30}\text{M}_{172}$. Similarly to the type-II clathrate, the cages in the type-III clathrate maybe filled with guests of different sizes or they may be partially vacant [28]. The first synthesis of two compounds of type-III clathrates were reported by *Bobev et al* in 2001 [34]. They have successfully synthesized and characterized a group with chemical formula of: $\text{Cs}_{30}\text{Na}_{(1.33x-10)}\text{Sn}_{(172-x)}$ and $\text{Cs}_{13.8(1)}\text{Rb}_{16.2(1)}\text{Na}_{(1.33x-10)}\text{Sn}_{(172-x)}$ where $x \approx 9.6$.

The two new compounds of ideal formula of $A_{30}Tt_{172}$ are found to be isostructural with inclusion compounds of the clathrate-III type such as $[(Br_2)_{20}\blacksquare_{10}](H_2O)_{172}$ and $[(CH_3OCH_3)_{20}\blacksquare_{10}](H_2O)_{172}$ where “ $\blacksquare$ ” denotes a vacancy [34]. These type-III clathrates exhibited a complete occupation of all of the polyhedral cages by Na alkali atoms and have some vacancies in the Sn framework. In this structure, Na plays an unusual role when partially filling up the framework vacancies.

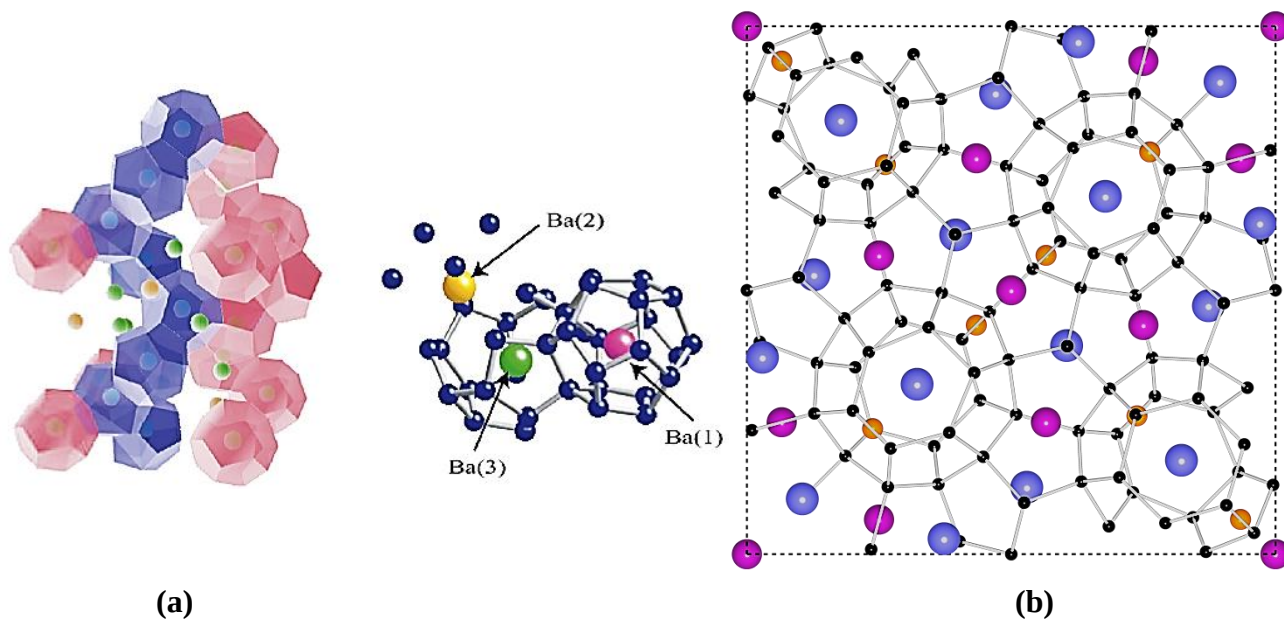


Figure I.4: 3D polyhedral representation of type-III silicon clathrate $Ba_{30}Si_{172}$ (a) by Tamegai *et al* [35] , (b) a (001) plane view.

I.3.4. Type-VII clathrate

The crystalline structure of the type-VII clathrates is initially formed from only one type of truncated-octahedron, which are polyhedral cages composed of six rectangles (squares) and six 6-fold rings normally symbolized as $[4^6 6^8]$. This class of clathrates crystallizes in the cubic space group $Im\bar{3}m$. In both reported crystal structures of clathrate-VII, phosphorus and transition metal atoms are segregated over separate crystallographic framework positions. This makes the square faces of the truncated-octahedron equivalent, and it leads to a reduction of the symmetry from cubic to tetragonal, i.e. $I4/mmm$ [19, 20]. At temperatures below 370K, the clathrate-VII $BaNi_2P_4$ additionally distorts down to orthorhombic, $Immm$ symmetry. The possible driving forces for this tetragonal-to-orthorhombic transition were discussed by Mewis *et al.* [20] and Hoffmann *et al.* [71]. Interestingly, the twisted clathrate has no analogues in gas hydrate chemistry. The two examples of twisted clathrates, $SrNi_2P_4$ and $BaCu_2P_4$ [18, 21], are based on late transition metals and phosphorus,

similar to the known structures of clathrate-VII, BaNi₂P₄ and BaPd₂P₄. The crystal structure of the twisted clathrate can be described as a tiling of space with unique 24-vertex polyhedra, referred to as twisted Kelvin cells (Fig. 2b). In the twisted clathrate, M₈P₁₆ polyhedra have 4 square-, 4 pentagonal-, and 6 hexagonal-faces, [445466] (Figs. 2 b and 7 right). According to O’Keeffe and Delgado-Friedrichs, this is one out of 10 of the possible 14-faced polyhedra which are capable of tiling space isohedrally [16].

I.3.5. Type-VIII

Type-VIII silicon clathrate with the same chemical formula as for the type-I phase (allotropic forms of the same clathrate compound), crystallizes in the body-centered cubic space group I4-3m (#217). The main framework of type-VIII clathrate is formed by combination of only one type of strongly-distorted dodecahedral cages (S₂₃), the host atoms of silicon occupy four Wyckoff positions: 2a, 12d, 24g and 8c, whereas, the guest atoms M occupy the 8c sites. Figure III.5 shows the configuration of a unit cell of type-VIII M₈Si₄₆ silicon clathrate. More details of this structure related to our subject are given in the chapter V [36].

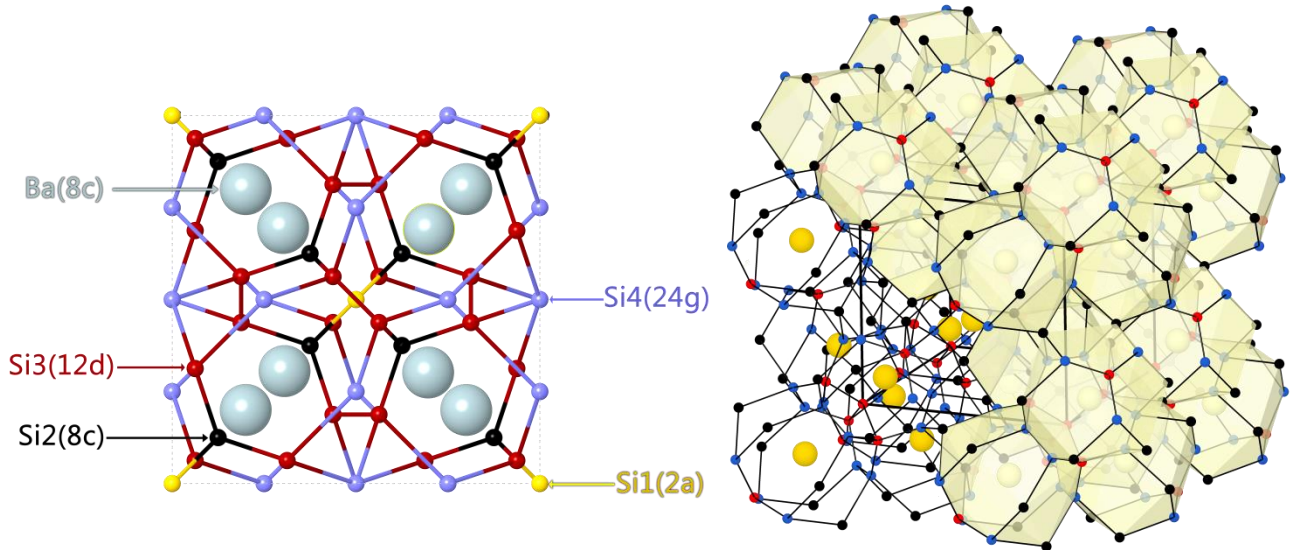


Figure III.5: Type-VIII silicon clathrate X₈Si₄₆ [36]

I.3.6. Type-IX

In type-IX clathrate (space group $P4_132$), pentagonal dodecahedra are the main forming cages, they share their pentagonal faces to form a sort of helical chains. The unit cell of this clathrate contains 100 host atoms, with eight guest atoms inside the pentagonal dodecahedra. Other open voids in the structure can host 16 up to 24 cations, and a general formula can be written as

$X_8Y_x[M_{100}]$, where $16 < x < 24$. The lowest content ration of guest atoms, $x = 16$, was observed in the Si $Ba_{24}Si_{100}$ [37] and Ge-based $Ba_{24}Ge_{100}$ [38] type-IX clathrates. In type-IX clathrates, part of the atoms in the framework are three-coordinated, while in all other previously discussed clathrates, all framework atoms are tetra-coordinated if no framework vacancies are present [28].

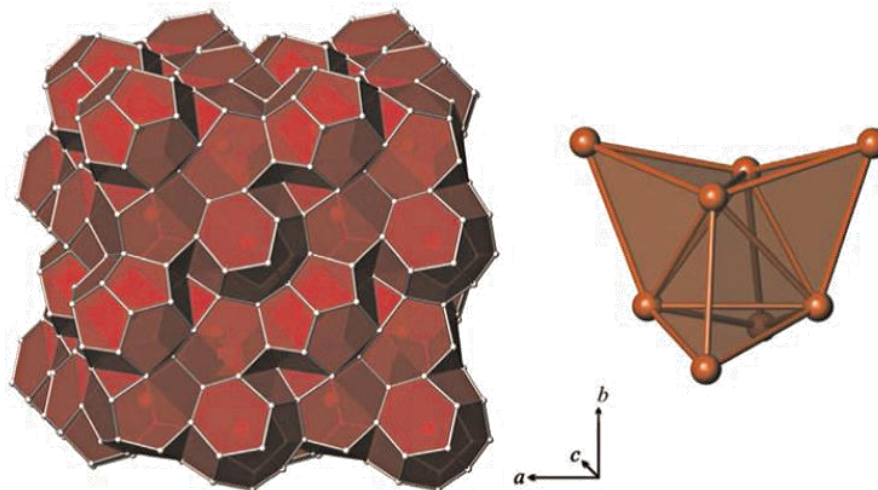


Figure III.6: Type-IX clathrate structure $X_8 Si_{100}$ [28]

I.4. Guest atoms ‘endohedral-confined’

In order to form the particular cage-like clathrate structure, the most important component is certainly the guest atom; guest atoms are directly responsible of allowing the formation of clathrates phases, under appropriate conditions of temperature and pressure. Thus, only groupe1 and group2 atoms (alkali-metal and earth-alkaline) are able to be confined. Endohedral atoms of group 1 or 2 are known to form metallic like compounds in their pure states, but unlike other metals, particular electronic configurations of their atoms is what makes them so easy to behave like guests and easily entrapped within inorganic group 14 cages. in contrary, group 3 transition metal in their reaction with silicon for example, even under such condition of pressure and temperature fails to form into clathrates, and gives silicide compounds instead, in order to better understand and to distinguish between transition, and alkali or alkaline earth metals we have to know the difference. Table lists the main differences between group-1, group-2 and group-3 transition metals.

I.5. Conclusion

In this chapter we briefly reviewed the history and the possible types of silicon clathrates, particular attention will be given to the type-I and type-VIII as the main materials for our study.

Next chapter will outline the theoretical background and the Density Functional theory, which is the base of our first-principles calculations throughout this work.

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CHAPTER II

Theoretical Background: Density Functional Theory

Abstract

This chapter presents a short glance of the theoretical framework of ab-initio calculations used throughout this thesis. In our case, the Density Functional Theory (DFT) was the background theory of the calculations. It uses the fundamental laws of quantum mechanics as foundation for the computations where the Schrödinger's equation for a many-body system is solved using strong approximations. Hence, the equations of KOHN and SHAM are introduced along with the LDA and the GGA approximations, and the two methods of representation of the wave function: the potential pseudo method and the all-electron method are detailed and discussed. Then, the DFT codes used in this thesis i.e. CASTEP, which uses plane-wave pseudopotential codes and employ periodic boundary conditions, is presented.

II.1. Introduction

Over the past few decades, density functional theory (DFT) has been the most successful and widely used method in condensed-matter physics, computational materials science (including quantum physics and chemistry) and biology to describe the main properties of condensed matter systems, which include not only standard bulk materials but also complex materials such as molecules, proteins, interfaces, 2D structures, surfaces and nanoparticles. The main idea of DFT is to describe a many-body interacting system through its particle density instead of its wave function or energy. Its significance is to reduce the $3N$ degrees of freedom of the N -body system to only three spatial coordinates through its particle density. It's mainly based on the well-known Hohenberg-Kohn (HK) theorem [1] which stipulates that all properties of a system can be considered to be unique functionals of its ground state density. Together with the Born-Oppenheimer (BO) approximation [2] and Kohn-Sham (KS) [3], practical accurate DFT calculations have been made possible via approximations for the so-called exchange and correlation potential (XC), which describes the effects of the Pauli principle and the Coulomb potential beyond a pure electrostatic interaction of the electrons. Since it is impossible to calculate the exact XC potential (by solving the

many-body problem exactly), a common approximation is the so-called local density approximation (LDA) which locally substitutes the XC energy density of an inhomogeneous system by that of a homogeneous electron gas evaluated at the local density. In most cases, the results of DFT calculations agreed quite fairly with experimental data, especially with the development of better XC energy approximations since the mid-1990s. Also, the computational costs were relatively low compared to traditional ways which were based on the complicated many-electron wave function, such as Hartree-Fock theory and its descendants. Despite the progresses of the DFT, there are still some difficulties in using it to accurately describe the intermolecular interactions, the charge transfer excitations, the transition states, the global potential energy surfaces and some other strongly correlated systems, and in the calculations of bandgaps of some semiconductors.

II.2. Density Functional Theory DFT

II.2.1.Introduction

The density functional theory aims to describe an electron-nucleus system considering the density $n(r)$ as a basic variable [4]. L. H. Thomas and E. Fermi were the first to write the energy as a function of density in 1921 [5]. In their model, the electronic interactions are treated classically and the kinetic energy is calculated supposing a uniform electronic density. This model was improved by P. A. Dirac with adding an exchange term. After that, J.C. Slater proposed in 1951 a model based on studies of uniform electron gas (cloud) augmented with a local potential [6]. This method named: Hartree-Fock-Slater or $X\alpha$ was used for solid state physics during the 1970s [4]. The DFT has really started with the fundamental theorems of Hohenberg and Kohn in 1964 [1]; they have established a functional relation between energy of the fundamental state of an electronic system and its density. In spite that the first successful works on using DFT for calculating electronic structures of solid only emerged in the 1990s with the development of exchange and correlation functionals. The most powerful and robust ones were used for large systems were introduced into the GAUSSIENNE software [7], since there, many packages appeared including open-source or commercial codes, are all reliable and has given satisfying results. Finally we have to mention that the Nobel price of physics of 1998 was attributed to KOHN and POPLÉ jointly for developing the DFT theory and its impact on theoretical investigation and prediction of materials [8, 9].

II.2.2. Basic principles of the DFT

II.2.2.A. The Schrödinger's equation

In 1926, Austrian physicist Erwin Schrödinger has formulated his famous equation, in the aim of describing the evolution of a quantum state of a system with time. One simple form of the Schrödinger equation, more precisely, the famous time independent, nonrelativistic Schrödinger equation:

$$\mathbf{H}\psi = E\psi \quad \text{II.1}$$

Where, $\mathbf{H}$ is the Hamiltonian operator and ψ is a set of solutions, or “eigenstates”, of the Hamiltonian. Each of these solutions, ψ_n , has an associated eigenvalue, E_n , which is a real number that satisfies the eigenvalue equation. The detailed formula of the Hamiltonian of a physical system depends on the properties being described by the Schrödinger equation. There are several well-known examples like the particle in a box or a hydrogen atom where the Hamiltonian has a simple form and the Schrödinger equation can be solved exactly, however, for complex multi atom systems, the resolution of this equation become more and more complex, such in our systems where multiple electrons are interacting with multiple nuclei. In this case, a more complete description of the Hamiltonian is:

$$\mathbf{H} = \mathbf{T}_e + \mathbf{V}_{eN} + \mathbf{V}_{ee} + \mathbf{T}_N + \mathbf{V}_{NN} \quad \text{II.2}$$

Where :

- $\mathbf{T}_e$: kinetic energy of electrons
- $\mathbf{V}_{eN}$: potential energy of electrons
- $\mathbf{V}_{ee}$: electrostatic repulsion energy between electrons
- $\mathbf{T}_N$: kinetic energy of nucleus
- $\mathbf{V}_{NN}$: electrostatic repulsion energy between nuclei

Replacing the above quantities by their detailed forms, the Hamiltonian become:

$$\mathbf{H} = \underbrace{-\sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2}_{\mathbf{T}_e} - \underbrace{\sum_{i=1}^N \sum_{j=1}^n \frac{e^2}{4\pi\epsilon_0} \frac{Z_j}{r_{ij}}}_{\mathbf{V}_{eN}} + \underbrace{\sum_{i=1}^N \sum_{k>i}^N \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ik}}}_{\mathbf{V}_{ee}} - \underbrace{\sum_{j=1}^n \frac{\hbar^2}{2M_j} \nabla_j^2}_{\mathbf{T}_N} + \underbrace{\sum_{j=1}^n \sum_{l>j}^n \frac{e^2}{4\pi\epsilon_0} \frac{Z_j \cdot Z_l}{R_{jl}}}_{\mathbf{V}_{NN}} \quad \text{II.3}$$

Where: $\hbar$ is Planck's constant, m_e is the mass of electron, e is the charge of electron, M_j is the mass of a nucleus j , r_{ij} is the distance between an electron i and a nucleus j , R_{jl} is the distance between a nucleus j and a nucleus l of which the respective charges are Z_j and Z_l , ∇_i is the Laplacian of the i^{th} particle (electron or nucleus) defined as:

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \quad \text{II.4}$$

II.2.2B. Atomic units

In order to facilitate the calculation, it is more convenient to work with atomic units (a.u) instead of the international system units (IS), these units are listed in Table II.1.

Table II.1 Atomic units of the main quantities used in calculations

Grandeurs	Symbol	IS units	Atomic unit (a.u)
Electron rest mass	m_e	$9,109.10^{-32}$ kg	1 a.u
Elementary charge	e	$-1,602.10^{-19}$ c	1 a.u
Reduced Planck's constant	$\hbar$	$1,055.10^{-34}$ j.s	1 a.u
Length	$a_0 = \frac{4\pi\epsilon_0 \cdot \hbar}{m \cdot e^2}$	$0,529.10^{-10}$ m	1 a.u =1(Bohr)
Energy	$E_0 = \frac{\hbar^2}{m \cdot a_0^2}$	$4,359.10^{-18}$ j	1 a.u =1(Hartree)

Using these units, the Hamiltonian can be simplified as:

$$H = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{j=1}^n \frac{Z_j}{r_{ij}} + \sum_{i=1}^N \sum_{k>i}^N \frac{1}{r_{ik}} - \sum_{j=1}^n \frac{1}{2M_j} \nabla_j^2 + \sum_{j=1}^n \sum_{l>j}^n \frac{Z_j \cdot Z_l}{R_{jl}} \quad \text{II.5}$$

II.2.2.C.The Many-Body System and Born-Oppenheimer (BO)

Approximation

It was in 1927 that Born and Oppenheimer proposed a simplification to the resolution of the Schrödinger equation (II.1), and this by separating the electronic part from the nuclear part in the wave function. This approximation is essentially based on the fact that the electrons move much faster than the nuclei, this being due to the large mass of the proton relative to that of the electron

(about 1836 times). As a result, the electrons react almost instantaneously to a change in the positions of the nuclei [2]. The electrons then adiabatically follow the displacement of the nuclei. That means, if a system nuclei have a given distribution $\mathbf{R}$, only the electronic energy contribution $E(\mathbf{R})$ to the total energy E is needed to know the properties of that system. This amounts to solving two Schrödinger equations, one for the nuclear part and the other for the electronic part. The system's wave function, a solution of the Schrödinger equation in the Born and Oppenheimer approximation, can therefore be written as a product of two functions:

$$\psi(\mathbf{r}, \mathbf{R}) = \psi_e(\mathbf{r}, \mathbf{R}) \cdot \phi(\mathbf{R}) \quad \text{II.6}$$

Where: Where $\phi(\mathbf{R})$ is the nuclear wave function, $\psi_e(\mathbf{r}, \mathbf{R})$ is the electronic wave function corresponding to a set of $\mathbf{R}$ positions of the fixed nuclei, $\mathbf{r}$ and $\mathbf{R}$ being the positions of the electrons and nuclei respectively.

We can then write the Hamiltonian $\mathbf{H}$ in the form:

$$\mathbf{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{j=1}^n \frac{1}{M_j} \nabla_j^2 + \sum_{j=1}^n \sum_{l>j}^n \frac{\mathbf{Z}_j \cdot \mathbf{Z}_l}{R_{jl}} + V(\mathbf{r}, \mathbf{R}) \quad \text{II.7}$$

Where $V(\mathbf{r}, \mathbf{R})$ is a potential depending on the position of the electrons and nuclei, an electronic operator $\mathbf{H}_e(\mathbf{r}, \mathbf{R})$ appears of the form:

$$\mathbf{H}_e = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + V(\mathbf{r}, \mathbf{R}) \quad \text{II.8}$$

It can be shown, through some approximations, that if we replace the expression (II.6) in the Schrödinger equation (II.1), we obtain after separation of the electronic and nuclear parts:

$$\mathbf{H}_e(\mathbf{r}, \mathbf{R}) \psi_e(\mathbf{r}, \mathbf{R}) = E(\mathbf{R}) \psi_e(\mathbf{r}, \mathbf{R}) \quad \text{II.9}$$

The wave function $\psi_e(\mathbf{r}, \mathbf{R})$ is a proper function of the electronic operator $\mathbf{H}_e$ with the eigenvalue $E(\mathbf{R})$, for positions $\mathbf{R}$ of the fixed nucleus. By solving the equation (II.9) for several successive positions of the nuclei, we obtain a function of $\mathbf{R}$ as follows:

$$E_{B.O}(\mathbf{R}) = E(\mathbf{R}) + \sum_{j=1}^n \sum_{l>j}^n \frac{\mathbf{Z}_j \cdot \mathbf{Z}_l}{R_{jl}} \quad \text{II.10}$$

Which represents the Born-Oppenheimer energy of the system as a function of positions of the fixed nuclei $\mathbf{R}$.

Born and Oppenheimer have also shown that the motion of atoms is governed by a Schrödinger-type equation where the potential depends on the electronic energy evaluated through equation (II.6).

$E_{B.O}(\mathbf{R})$ thus plays the role of a potential energy for the movement of the nuclei. For the resolution of the electronic part, considering that the behavior of the electrons is practically not modified by the weak displacements of the nuclei which are supposed to be fixed in their instantaneous position, the Hamiltonian in the approximation of Born- Oppenheimer is limited to electronic components only:

$$H_e = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{j=1}^n \frac{Z_j}{r_{ij}} + \sum_{i=1}^N \sum_{k>i}^N \frac{1}{r_{ik}} \quad \text{II.11}$$

We note that the last term: $\sum_{i=1}^N \sum_{k>i}^N \frac{1}{r_{ik}}$ is a bi-electronic operator while the first two are mono-electronic operators, which poses a subsequent difficulty for the processing of the function ψ_e that we will henceforth designate solely by the letter ψ .

II.2.2.D. Hohenberg-Kohn Equations

Under the light of previous Born-Oppenheimer simplifications and the approximations by Hartree-Fock (skipped here for simplification matters, but the reader can refer to [10] for further information). Both theorems of Hohenberg and Kohn formulated in 1964 have permitted giving coherence to models developed on the basis of theories proposed by Thomas and Fermi in the late 1930s [1].

II.2.2.D.1. 1st theorem

“The ground-state energy from Schrödinger’s equation is a unique functional of the electronic density”.

The total energy (E) of fundamental state of an electronic system is only a function of the particles density $n(\vec{r})$ for a given external potential $V_{ext}(\vec{r})$.

This theorem means that it is sufficient to know the electron density to determine the total energy of the system. Consequently, the energy of the ground state can be written as a function of the electron density

$$E[n(\vec{r})] = \langle \Psi | H | \Psi \rangle = F[n(\vec{r})] + \int V_{ext}(\vec{r}) \cdot n(\vec{r}) \cdot dr \quad \text{II.12}$$

$$F[n(\vec{r})] = T_e[n(\vec{r})] + V_{ee}[n(\vec{r})] \quad \text{II.13}$$

Where: T_e is the kinetic energy; V_{ee} represents the electron-electron interaction energy. F is a universal functional of the density (Hohenberg and Kohn functional).

Then the DFT reduced the problem of N_e body to the determination of a three-dimensional function $n(\vec{r})$.

II.2.2.D.2. 2nd theorem

“The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger’s equation”.

There exists a universal functional $E[n(\vec{r})]$ expressing the total energy as a function of the electronic density $n(\vec{r})$, valid for any external potential $V_{ext}(\vec{r})$. The energy of the fundamental state of the system is the value that minimizes this functional and the corresponding density $n_0(\vec{r})$ is the exact density of the ground state.

$$E[n_0] = \text{Min}_n (E[n]) \quad \text{II.14}$$

All other properties are also a functional of this density. The ground state energy of an electronic system in an external potential is then calculated by the variational method [11]. The major problem of this approach is that we do not yet know the functional $F[n]$ of equation II.13.

II.2.2D.3. The Kohn-Sham equations

In 1965, Kohn and Sham proposed replacing the actual interacting particle system with a non-interacting dummy system, which has the same electron density as the real system. In this case the operator of the kinetic energy is known and easy to calculate since one is in front of free electrons. The exact functional energy takes the following form:

$$E[n] = T_0[n] + V_H[n] + V_{ext}[n] + E_{xc}[n] \quad \text{II.15}$$

Avec :

$$V_H = \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr dr' : \text{is the Hartree energy.}$$

$$V_{ext}[\rho] = \int \frac{Z_i n(r)}{|r-R_i|} dr : \text{is the nucleus-electron attraction potential energy.}$$

$$E_{xc}[n] = (T - T_0) + (V_{ee} - V_H) : \text{is the Exchange and Correlation Energy XC.}$$

$T_0[n]$: is the fundamental kinetic energy of the system.

We can then write the equations of Kohn-Sham as:

$$H_{KS} \Psi_i = \varepsilon_i \Psi_i \quad \text{II.16}$$

$$(T_0 + U_H + U_{XC} + U_{ext})\Psi_i = \varepsilon_i \Psi_i \quad \text{II.17}$$

With

$$n(\vec{r}) = \sum_{i=1}^{N_e} |\Psi_i(\vec{r})|^2 \quad \text{II.18}$$

Where: $\Psi_i(\vec{r})$ is the wave function of the i^{th} electron.

II.3. DFT Approximations

As described above, the DFT theory is, at the stage of the Kohn-Sham equations, a perfectly exact theory (apart from the Born-Oppenheimer approximation and the numerical approaches) insofar as the electron density which minimizes the energy total is exactly the density of the Ne interacting electron system. However, the DFT remains inapplicable because the exchange-correlation potential remains unknown. It is therefore necessary to approximate this potential. Two main types of functionalities are part of this approach: the LDA (for Local Density Approximation) and the GGA (Generalized Gradient Approximation).

II.3.1. Local density approximation (LDA)

The main difficulty in developing the Kohn-Sham's formalism lies in the construction of exchange-correlation XC functionals. The local density approximation known as "LDA" stipulates, as a first approximation, that the density can be considered as being locally constant, and the value of the functional at a point of space depends only on the electronic density n at this point. The results obtained are only correct if the electron density does not undergo inhomogeneous zones [7]. We can then define the exchange-correlation energy in the following way:

$$E_{xc}[n] = \int n(\vec{r}) \varepsilon_{xc}[n] d^3r \quad \text{II.19}$$

It is based on the model of uniform electron gas. It was calculated by Ceperley and Alder using Monte-Carlo techniques [12], and is parameterized by Perdew and Zunger [13]. This technique makes it possible to parameterize an expression of the functional from different values of $n(\vec{r})$.

Moreover, if we divide the exchange energy and correlation into two (exchange energy ϵ_x plus correlation energy ϵ_c) such that:

$$E_{xc} = \epsilon_x + \epsilon_c \quad \text{II.20}$$

Several forms of exchange energy ϵ_x and correlation ϵ_c have been proposed for the calculation of E_{xc} .

In practice, the LDA method is more efficient than the Hartree-Fock calculations. However, it is generally observed that this approximation tends to underestimate the bonds lengths in the molecules and, consequently, to overestimate the binding energies. Moreover, it is very common that the activation barriers of chemical reactions are largely underestimated. On the other hand, the vibration frequencies are generally in good agreement with experiments (the difference is often less than 5%). Since 1985, enormous efforts have contributed to the improvement of exchange and correlation functionals. This work has led to a second generation of functionals including the inhomogeneity of the electronic density: these functionals therefore take into account the electronic density as well as its gradient.

II.3.2. Generalized gradient approximation (GGA)

Despite the simplicity of the LDA, it has yielded reliable results in many cases, but there were many cases where it contradicted experience [14]. For this reason the gradient of electronic density has been introduced leading to a generalized gradient approximation GGA where the energy E_{xc} is as a function of the electron density and its gradient:

$$E_{xc}^{GGA}[n] = \int n(\vec{r}) \epsilon_{xc}[n, \nabla n] d^3r \quad \text{II.21}$$

- The exchange part is calculated on the same basis as for LDA, but adding a factor of improvement depending on the gradient.
- The correlation part takes into account the parameterization of the LDA by adding:
 - ♣ a new parameterization for the gradient. This is the case of functional B (Becke88) [15], PW (Perdew-Wang) [16] or even mPW (modified Perdew-Wang);
 - ♣ a more theoretical term using only fundamental constants, such as the PBE (Perdew-Burke-Ernzerhof) functional [17].

Semi-empirical GGA obtain very good results for particular systems such as small molecules, but fail in this case to reproduce the behavior of electrons delocalized from a homogeneous electron gas (as for example in a metal).

II.3.3. Comparison to experimental results

Despite the apparent differences of the two approximations we have seen, the calculations made using LDA or GGA give results in good agreement with the experiment generally.

It is interesting to note that the error of both functionals versus experience follows some trends that we can summarize in Table II.3.

We can also notice that the difference of result between these two methods depends on the physical property to be investigated, but that their relative position is relatively little changed whatever the system: the lattice parameter predicted by LDA will be for example always lower of some percents to that predicted by GGA [14].

Table II. 2: *Tendencies of the exchange and correlation functionals GGA and LDA*

	LDA	GGA
Lattice parameter	Underestimate (<10%)	Overestimate (<5%)
Bandgap	Underestimate	Underestimate
Young's modulus	Overestimate	Underestimate

II.4 – Calculation methods of electronic structures

The Kohn and Sham equations are solved by several numerical methods. Among these methods are the full potential linearized augmented plane wave (FP-LAPW) method and the pseudopotential (PP) method, which will be presented in the following section.

II.4.A – Pseudopotential methods (P.P)

The valence electrons can determine almost all the physical properties of materials by forming chemical bonds and relocating to the solid. The interaction of the valence electrons with the nucleus and core electrons can be replaced by an effective potential, much less attractive than the potential created by the nucleus. This effective potential is called “pseudopotential” (Figure II.1).

The pseudo potential thus makes it possible to reduce the number of electrons to be taken into account in the calculation and also to reduce the number of plane waves necessary to describe

the wave functions of the solid. This leads to reducing the calculation volume and shortening the execution time.

Figure (II.1) shows the variations of the wave and potential function in the two atomic regions as a function of (r) distance from the nucleus, and the correlation that exists between the two methods (FP and PP) from a certain distance from the core, this distance is known as the cutoff radius ($R_{cut-off}$). Throughout this thesis we will use the pseudo potentials proposed by Vanderbilt within the Ultrasoft approach [18], generated under the two approximations GGA-PBE and GGA-BLYP, and available for most elements of the periodic table.

Since valence electrons behave almost like free electrons in metals, and a solid is modeled by a periodic arrangement of atoms, the natural basis for numerical calculations is thus the plane wave base. Many methods have been proposed to generate pseudopotentials; among these methods we quote the method of Vanderbilt [18]. The pseudopotential must satisfy the following criteria:

- It must take into account the interaction with the screened nucleus, the electronic repulsion (Hartree), the repulsion due to the Pauli principle and the exchange and correlation interaction.
- The relativistic effect of the core electrons for heavy atoms.
- It must ensure the continuity of the wave function.

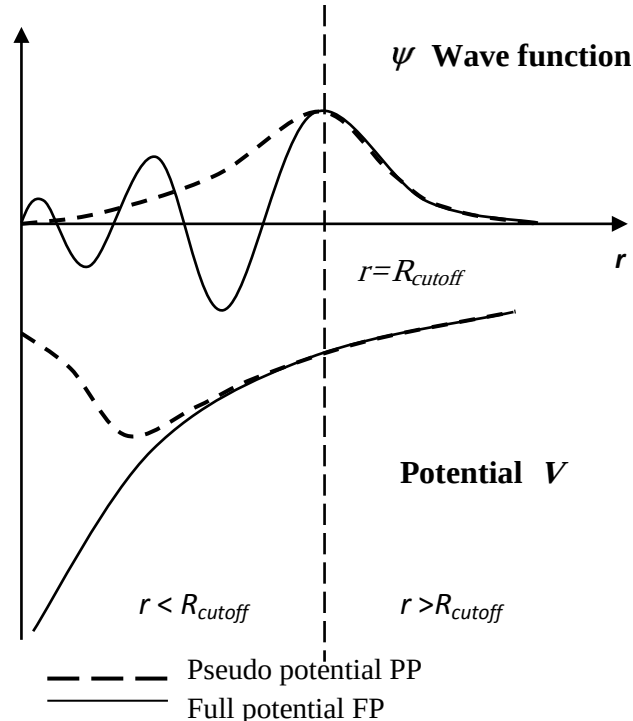


Figure II.1 : *variation of the wave function and the potential in the two atomic regions*

II.4.B – The full-potential method (FP-LAPW)

FP-LAPW: Full Potential Linearized Augmented Plane Wave, this method is based on the linearized augmented plane waves [10]. In this method the atomic space is divided into two regions, the first represents the spheres (α) centered at the nuclei of the atoms, called the Muffin tin spheres, see Figure II.2.

The basic functions in this region are linear combinations of the radial functions $U_l(r)$, in turn, these radial functions are developed in series of Taylor, around the value E_0 of the total energy at ground state, for each sphere (α) according to the following expression [10,18].

$$U(r, E) = U(r, E_0) + (E - E_0)\dot{U}(r, E_0) + (E - E_0)^2\ddot{U} + \dots \quad \text{II.22}$$

By limiting to the first two terms, the basic functions will therefore be linear combinations of the radial functions $U(r, E_0)$, and their derivatives $\dot{U}(r, E_0)$ multiplied by the harmonics $Y_{l,m}(r)$. The second region is what remains of the atomic space, called the interstitial region where the crystal wave functions are developed in a plane wave base.

$$\psi(r, E) = \begin{cases} \frac{1}{\sqrt{\Omega}} \sum_G C_G \exp i(K + G) \cdot r & r \in II(r) R_\alpha \\ \sum_{l,m} (A_{l,m} U_l(r, E_0) + B_{l,m} \dot{U}_l(r, E_0)) Y_{l,m}(\theta, \phi) & r \in I(r) R_\alpha \end{cases} \quad \text{II.23}$$

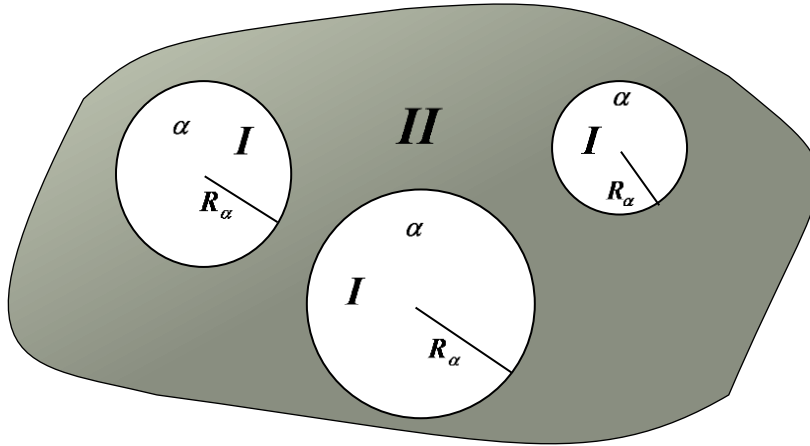


Figure II.2: The two parts of the atomic space, (I) MT spheres, (II) interstitial region.

When calculating the Eigen functions ψ_K^n in the region (I), we must set a criterion on the value of l , for limited the number of basic functions.

The advantages of this method can be summarized as follows:

- Linearly augmented plane waves in the region of the spheres Muffin-tin.
- Plane waves in the interstitial region.
- The energy of the bands at points K is obtained by simple diagonalization.
- The discontinuity problem is eliminated by introducing the derivative of the function with respect to the energy, which guarantees the non-decoupling of the plane waves with the wave functions.
- The base is more flexible because there is more variational freedom.

II.5 – Calculation techniques

II.5.1 –Bloch's theorem

For an infinite crystalline solid on which one imposes conditions on the periodic limits of Born-Von Karman [19], the resolution of the Kohn-Sham equations returns to find the Eigen functions which are subjected to an external potential V_{ext} which has the periodicity of the crystal, such as:

$$V_{\text{ext}}(\vec{r}) = V_{\text{ext}}(\vec{r} + \vec{a}) = V_{\text{ext}}(\vec{r} + s\vec{a}) \quad \text{II.24}$$

With: a is the lattice parameter, and s is an integer.

Bloch has demonstrated [20] that the Eigen functions of a Hamiltonian that contains such an external potential have the form:

$$\psi_{n,\vec{K}}(\vec{r}) = \frac{1}{\sqrt{L\Omega}} u_n(\vec{K}, \vec{r}) e^{i\vec{K} \cdot \vec{r}} \quad \text{II.25}$$

With: $u_n(\vec{K}, \vec{r})$ is w function that has the periodicity of the crystal, where:

$$u_n(\vec{K}, \vec{r}) = u_n(\vec{K}, \vec{r} + \vec{a}) = u_n(\vec{K}, \vec{r} + s\vec{a}) \quad \text{II.26}$$

L : number of lattices in the crystal

Ω : Lattice volume

n : principal quantum number of energy band

$\vec{K}$: Wave vector of the first Brillouin zone

The wave-function in (II.44) is decomposed into Fourier series

$$\Psi_{n,\vec{K}}(\vec{r}) = \frac{1}{\sqrt{L\Omega}} \sum_{\vec{G}} C_{n,\vec{K}}(\vec{G}) e^{i(\vec{K}+\vec{G})\cdot\vec{r}} \quad (\text{II.27})$$

With: $\vec{G}$ is a reciprocal vector.

We inject the function (II.26) into the equation K-S (II.15), we obtain:

$$\left[T_0(\vec{K} + \vec{G}) + V_{ee}(\vec{G}) + E_{xc}(\vec{G}) + V_{ext}(\vec{G}) - \varepsilon_n(\vec{K}) \right] C_{n,\vec{K}}(\vec{G}) = 0 \quad (\text{II.28})$$

Where

$V_{ee}(\vec{G}), E_{xc}(\vec{G}), \text{ et } V_{ext}(\vec{G})$, are the Fourier transforms of: the Hartree potentials operators, the exchange-correlation, and the external potential respectively.

We can solve the equation (II-27) by means of a numerical diagonalization or we can use variational principles in order to adjust the $C_{n,\vec{K}}(\vec{G})$ coefficients to minimize the total energy.

II.5.2 – Sampling of the first Brillouin zone and the cut-off kinetic energy

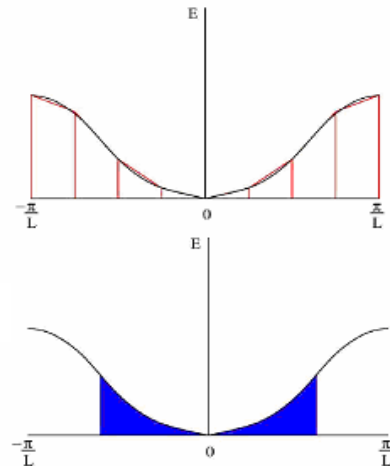
II.5.2.A – Sampling of the first Brillouin zone

To solve the equation (II-27), the Bloch's functions must be determined at all K-points of the first Brillouin zone BZ. The property of Bloch's functions is to vary very slowly in the vicinity of a point in the BZ that allows an easy sampling. Such sampling is often called “the choice of K-points”. The integral over all the space of BZ thus returns to the summation on these chosen K-points (Figure II-3).

$$E_{total} = \frac{1}{V} \int_{BZ} E(\vec{K}) d\vec{K} = \frac{1}{V} \sum_{\vec{K}} E(\vec{K})$$

$$\rho(\vec{K}) = \frac{1}{V} \int_{BZ} \rho_{\vec{K}}(\vec{r}) d\vec{K} = \frac{1}{V} \sum_{\vec{K}} \rho_{\vec{K}}(\vec{r})$$

Figure II.3 : Sampling of the first Brillouin zone BZ.



In principle we must use an infinite number of K-points for the exact calculation of the total energy, but in practice this number is finite due to the computation power limits (even in the latest supercomputers) and consequently introduces systematic calculation errors. We are here in front of two opposing ways, namely: to reduce the volume and calculation time or to improve the accuracy of calculations. Therefore a technical arrangement is required which consists of taking a finite number of k-points in each direction of the reciprocal network, which is increased each time to obtain a good convergence of the physical properties in question.

II.5.2.B – The cut-off kinetic energy E_{cut}

In principle we should use an infinite number of plane waves to represent the Bloch's waves of equation (II-27), but in practice, we have to truncate the series development. It is then restricted to plane waves whose kinetic energy is less than a predefined cutoff energy E_{cut} .

$$\frac{h^2}{2m}|K + G|^2 \leq E_{cut}. \quad (\text{II.29})$$

In practice, it is always necessary to test the convergence of the results with respect to the kinetic cutoff energy and with respect to the grid of K-points. We start the calculations by choosing a certain value of E_{cut} and then increase E_{cut} and repeat the same calculation until the magnitude we want to determine no longer varies at certain degree of precision upon our available computational resources.

II.6. The CASTEP and DMol³ codes

II.6.1- CASTEP

The Cambridge Serial Total Energy Package (CASTEP) [11, 21], As an important module in the Materials Studio software, it is a first-principles quantum mechanics program based on the density functional theory (DFT), is a powerful state-of-the-art quantum mechanics-based program developed specifically for solid-state materials science. CASTEP employs the density functional theory DFT plane-wave pseudo-potential method, which allows performing first-principles calculations to investigate the properties of crystals and surfaces in materials such as semiconductors, ceramics, metals, minerals, and zeolites. Typical applications involve studies of surface chemistry, structural properties, band structure, density of states, and optical properties.

CASTEP can also be used to study the spatial distribution of the charge density and wave functions of a system. Further details about this code can be found [here](#).

BIOVIA Materials Studio [CASTEP](#) is an ab initio quantum mechanical program employing density functional theory (DFT) to simulate the properties of solids, interfaces, and surfaces for a wide range of materials classes such as ceramics, semiconductors, and metals. First principle calculations allow researchers to investigate the nature and origin of the electronic, optical, and structural properties of a system without the need for any experimental input. Materials Studio CASTEP is thus well suited to research problems in solid state physics, materials science, chemistry, and chemical engineering where empirical models are lacking and experimental data may be sparse. In these areas, researchers can employ computer simulations to perform virtual experiments, leading to tremendous savings in costly experiments and shorter developmental cycles.

II.6.2. DMOL³

BIOVIA Materials Studio [DMoL³](#) is a modeling program that uses density functional theory (DFT) to simulate chemical processes and predict properties of materials both rapidly and accurately. Because Materials Studio DMoL³ can predict processes in gas phase, solution, and solid environments, it is broadly applicable to research problems in chemistry, pharmaceuticals, materials science, and chemical engineering, as well as solid state physics. Researchers can use the program to investigate the nature and origin of the chemical, electronic, and structural properties of a system without the need for any experimental input. Use Materials Studio DMoL³ to perform virtual experiments, leading to tremendous savings in costly experiments and shorter developmental cycles.

II.7. Conclusion

In this chapter, a historical overview of the functional theory of DFT density was presented. We have exposed the K-S equations and approximations that have been behind the development of the DFT, the latter which has allowed the progress that we know today ab-initio calculations.

The DFT is based on Hohenberg theorem and Kohn states that all the physical properties of the ground state of an electron gas depend only on its density. The formalism of Kohn and Sham makes it possible to take advantage of this theorem and calculate the total energy of an electron system. The two most used methods in the construction of the wave function and therefore the electronic density are the pseudopotential PP method and the FP-LAPW (all-electron) method. In this chapter

we have exposed the two approximations used in the practical calculations of exchange-correlation energy as, local approximations (LDA) and generalized (GGA).

The understanding of this theory is indispensable before starting any ab initio calculation. The two most used methods are the all-electron, and pseudopotential method was exposed. In this manuscript we use the last one that will be implemented in the CASTEP code.

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CHAPTER III

Computational details, preliminary DFT results

Abstract

This chapter is dedicated to the presentation and discussion of the first results of first-principles calculations based on the DFT. Clathrates in the type-I configuration with the chemical formula of $X_8\text{Si}_{46}$ ($X = \text{Ca}, \text{Ba}, \text{Na}, \text{Li}, \text{Cs}$ and Rb) were investigated at their fundamental equilibrium state. GGA-PBE functionals were used along this study as implemented in the CASTEP code available within the commercial package Materials studio. Results were confronted to the available theoretical and experimental literature.

III.1. Introduction

Silicon is the second abundant matter on the earth's crust behind Oxygen, (27%) [1]. The maturity and development of the high-tech of today is directly related to the understanding and the mastering of silicon's technology. Since the invention of the transistor by Shockley et al in 1954, silicon has emerged as the most used and the well-understood semiconductor, its technology is well controlled at the industrial level, its physical and chemical properties were deeply investigated during past decades. These advantages has made of silicon the most used semiconductor in the majority of high-tech devices of today, starting from microelectronic devices, micro-chips, transistors, to the widely used conventional solar cells. Photovoltaic market is still dominated by silicon technology; its low price, abundance and the higher life-time of the panels are the main reason for this dominance. However, it has a major handicap: its indirect band gap, which makes him a very bad light absorber. Facing this dilemma, scientists and researchers tried to overcome this problem by exploring other direct band gap materials, so far they have succeeded to obtain good yielding efficiencies using these materials in thin film solar cells, for example: chalcopyrite materials, but those materials are expensive, and some of them are rare, make their production at industrial level very slow. A solution which combines the advantages of silicon (abundance, mastered technology), and direct band gap material (good absorption, cheap deposition techniques, thin films), is suitable in order to achieve a good solar cell. For that purpose, the atomic structure of

the common diamond silicon will be changed in order to engineer the silicon's band gap to make it direct, and try to project this technic for use as absorber layer in solar cells. Besides its common diamond structure, which is used in photovoltaic devices, there exist other allotropes for silicon including clathrate structures. In this first report, type I silicon clathrates with X_8Si_{46} formula are studied. Silicon clathrates are cage-like enclosing materials with sp^3 hybridization. Type 1 silicon clathrate was first synthesis in 1965 by Kasper et al [2]. Since then; it's harvesting a great amount of interest, and witnessed deep experimental and theoretical investigations. This is due to its exceptional thermoelectric [3], and superconducting properties.

III.2. Computational procedures

This first part deals with electronic and structural properties of a range of type I silicon clathrates with chemical formula: X_8Si_{46} , where X represents the alkali metallic guest atom. We carry out a series of calculations upon systematic study, in which we'll vary increasingly the atomic radius of guest atoms according to their positions in the periodic table of elements as shown in Figure III.1 below.

1	H	2	He
3	Li	4	Be
5	B	6	C
7	N	8	O
9	F	10	Ne
11	Na	12	Mg
13	Al	14	Si
15	P	16	S
17	Cl	18	Ar
19	K	20	Ca
21	Sc	22	Ti
23	V	24	Cr
25	Mn	26	Fe
27	Co	28	Ni
29	Cu	30	Zn
31	Ga	32	Ge
33	As	34	Se
35	Br	36	Kr
37	Rb	38	Sr
39	Y	40	Zr
41	Nb	42	Mo
43	Tc	44	Ru
45	Rh	46	Pd
47	Ag	48	Cd
49	In	50	Sn
51	Sb	52	Te
53	I	54	Xe
55	Cs	56	Ba
57	La	58	Ce
59	Pr	60	Nd
61	Pm	62	Sm
63	Eu	64	Gd
65	Tb	66	Dy
67	Ho	68	Er
69	Tm	70	Yb
71	Lu	72	Hf
73	Ta	74	W
75	Re	76	Os
77	Ir	78	Pt
79	Au	80	Hg
81	Tl	82	Pb
83	Bi	84	Po
85	At	86	Rn
87	Fr	88	Ra
89	Ac	90	Th
91	Pa	92	U
93	Np	94	Pu
95	Am	96	Cm
97	Bk	98	Cf
99	Es	100	Fm
101	Db	102	Sg
103	Bh	104	Hs
105	Mt	106	Ds
107	Rg	108	Cn
109	Uut	110	Fl
111	Uup	112	Lv
113	Uus	114	Uuo

Figure III.1: Alkali metallic guest atoms in the periodic

For that purpose, first-principles calculations based on the famous DFT (Density Functional Theory) [4, 5] are solicited, the Cambridge Serial Total Energy Package (CASTEP) is used in this work [6]. For all our calculations, plane-wave basis Ultrasoft pseudopotentials are chosen [7]. GGA-PBE (Perdew-Burke-Erzenhorff) functional is selected to approximate the exchange and correlation energy [8]. The kinetic cut-off energy was fixed at 380 eV, after a convergence study considering a 10^{-5} eV tolerance criterion. The first Brillouin zone was sampled at 6x6x6 grid following the Monkhorst-Pack k-point scheme [9]. Initial lattice parameters of our compounds are taken from the literature. We carried out geometrical optimization for each structure using the BFGS-algorithm

(Broyden-Fletcher-Goldfarb-Shanno) [10-13], in order to minimize their total energy. Forces below 10^{-3} eV/Å are considered to be nil.

The electronic band structures and density of states were calculated for each material at its optimized state, the high symmetry directions in the Brillouin zone were set according to the path characterizing the space group.

Type I silicon clathrates (X_8Si_{46}), crystallize in the simple cubic space group $Pm\bar{3}n$. A unit cell of guest free type I silicon Si_{46} clathrate, and of sodium-doped clathrate Na_8Si_{46} are shown in Fig.III.2(a) and Fig.III.2(b) respectively.

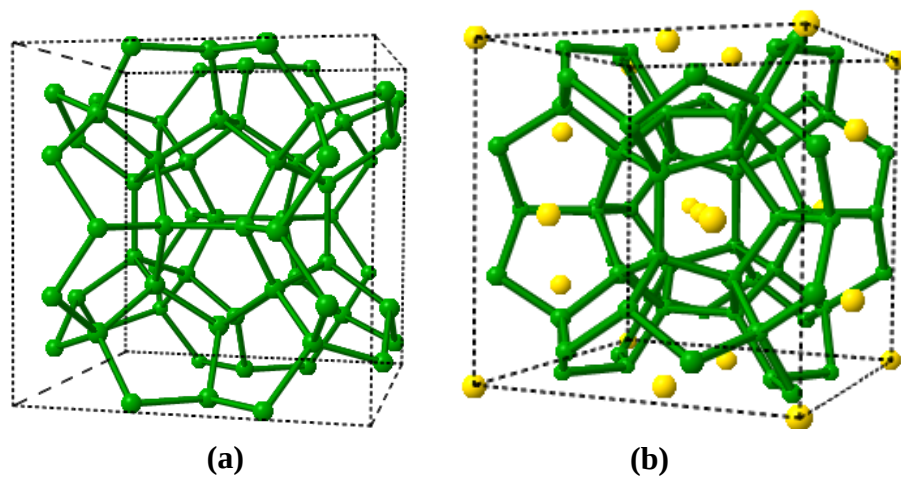


Figure.III.2. Crystalline structure of type-I silicon clathrates (Silicon are modeled in green balls and sticks, Na are modeled in yellow spheres)

We notice that even for large atoms as Rubidium or Barium, the lattice parameters are slightly changed regarding small guest clathrates, in fact, this was explained as larger atoms rather than expanding the framework of Si, they contribute to enhance the cohesively of the cages, and hence to strengthening its bonding. It was demonstrated that the enclosing large guest atoms in the empty cavities helps to enhance the structural stability of the Si framework, due to that the more space filling atoms help to maintain the framework integrity [14].

III.3.Results and discussion

Table1. Cell parameters and atomic position of Si-clathrate compounds

Compound	a (Å)	Host position (Si)	Guest position
Si₄₆	10,055	6c: (0,1835 0,1835 0,1835) 16i: (0 0,3077 0,1174) 24k: (0,25 0 0,50)	/ / /
Na₈Si₄₆	10,19	6c: (0,25 0 0,5) 16i: (0,1851 0,1851 0,1851) 24k: (0 0,310 0,116)	Na: 0,0 0,0 0,0 0,25 0,5 0,0
K₈Si₄₆	10,30	6c: (0,25 0 0,5) 16i: (0,183 0,183 0,183) 24k: (0 0,310 0,1160)	K: 0,0 0,0 0,0 0,25 0,5 0,0
Rb₈Si₄₆	10.27188	6c: (0,25 0 0,5) 16i: (0,183 0,183 0,183) 24k: (0 0,310 0,1160)	Rb: 0,0 0,0 0,0 0,25 0,5 0,0
Ca₈Si₄₆	10.23	6c: (0,25 0 0,5) 16i: (0,183 0,183 0,183) 24k: (0 0,310 0,1160)	Ca: 0,0 0,0 0,0 0,25 0,5 0,0
Sr₈Si₄₆	10.265	6c: (0,25 0 0,5) 16i: (0,183 0,183 0,183) 24k: (0 0,310 0,1160)	Sr: 0,0 0,0 0,0 0,25 0,5 0,0
Ba₈Si₄₆	10.328	6c: (0,25 0 0,5) 16i: (0,1854 0,1854 0,1854) 24k: (0 0,3061 0,1213)	Ba: 0,0 0,0 0,0 0,25 0,5 0,0

III.3.1- Structural properties

We show the calculated lattice parameters and atomic positions for each compound, in comparison with experimental values if available. It is well known that GGA approximation overestimate lattice parameters. Our results are showing a fair agreement with the literature, this lead us to confirm adequacy of the pseudopotentials chosen and the method of work.

III.3.2- Electronic properties

The predicted band structures of each material (Si₄₆, Na₈Si₄₆, Ca₈Si₄₆, Sr₈Si₄₆, Ba₈Si₄₆, K₈Si₄₆, Rb₈Si₄₆), and their total and partial densities of states are detailed bellow. For Si₄₆ the band structure plot shows a semiconducting type material, with a quasi-direct band gap of **1.273eV**. For X₈Si₄₆ clathrates, the band structures revealed a metallic character, in agreement with other works. This is due to the contribution of guest's valence electrons in the conduction band of the host framework. Hence, they contribute to rising of the Fermi level within the conduction band. It is evident that DFT-based calculations provide underestimated band gaps regarding the experimental values.

III.4. Si₄₆

Guest free silicon clathrate compound (Si₄₆), is the first material to be studied in this part. Figure III.4 illustrates (a) the charge density over the 001 plane, and (b) the crystalline structure of type-I guest-free Si₄₆.

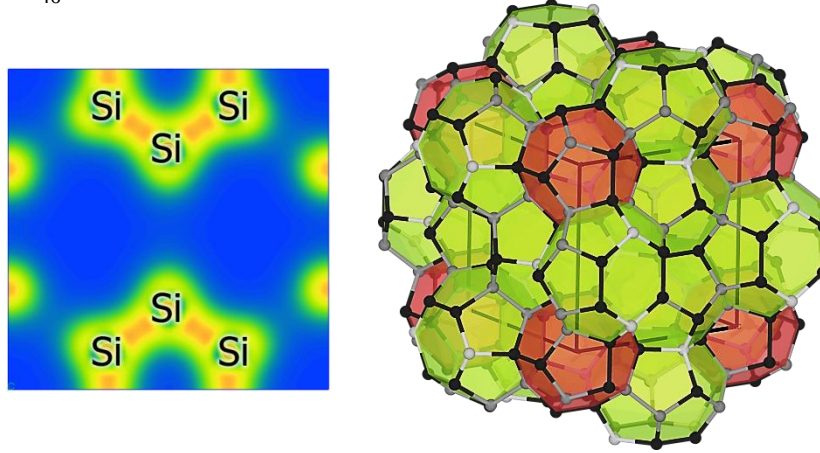


Figure III.3. (a) charge density over the 001 plane and (b) cage structure of Si₄₆

We compare our band structure (PP- PBE-GGA), with other calculated structures, (FP-LAPW LDA) by [14]. Concerning the band gap, in our calculation it is found to be equal to **1.273 eV**, slightly higher than the reference [14] (**0.967 eV**), and more close to the experimental value. Comparing both bands, we notice a fair agreement, with some change in allures; this is certainly due to the methods of calculations.

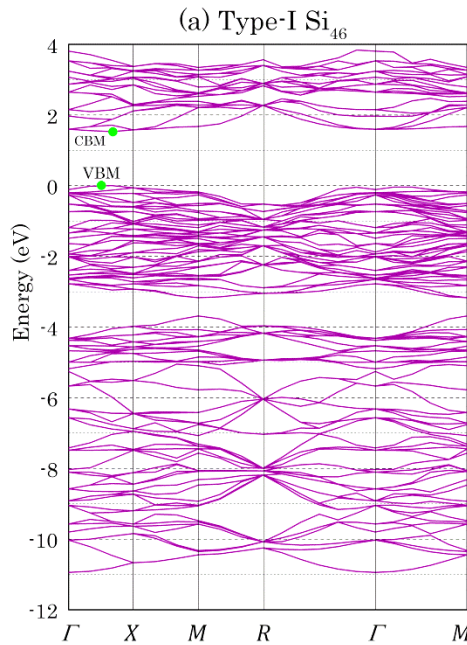


Figure III.4. Band structure of Si₄₆ calculated by GGA-PBE (Castep)

III.5. $\text{Na}_8\text{Si}_{46}$

Sodium doped silicon clathrate $\text{Na}_8\text{Si}_{46}$ is one of the well-known and popular clathrates compounds, it has been deeply investigated for its potentials as a thermoelectric material, using various experimental and theoretical technics, and we cite here some published works about this material:

Kurganskii *et al* [14], calculated the electronic structure and spectral properties of $\text{Na}_8\text{Si}_{46}$ clathrate, using DFT based LAPW (Linearized Augmented Plane Wave) method with LDA approximation. K.Biswas *et al* [15], calculated vibrational properties of Germanium based clathrate $\text{Na}_{16}\text{A}_8\text{Ge}_{13}$ (A=Rb, Cs). More recently, M.C.Blosser and G.S.Nolas from the University of south Florida (USA), synthesized $\text{Na}_8\text{Si}_{46}$ and $\text{Na}_{24}\text{Si}_{136}$ clathrates through bi-oxidation of Na_4Si_4 precursor from ionic liquid decomposition [16]. We will start with Na doped Si-clathrate, as sodium is the smallest radius among the chosen species. Atomic radius of Na is equal to 190 pm.

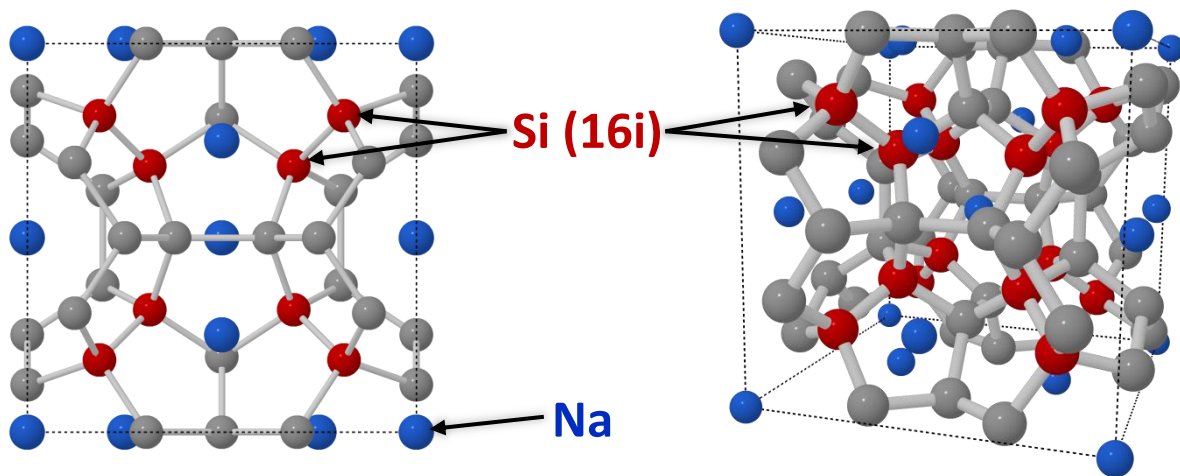


Figure.III.5. Crystalline structure of $\text{Na}_8\text{Si}_{46}$.

Total energy and structural optimization

The first step consists of calculating total energy, and optimizing geometry of the structure in order to minimize this energy and find the equilibrium parameters. The results of these operations are detailed in the table below.

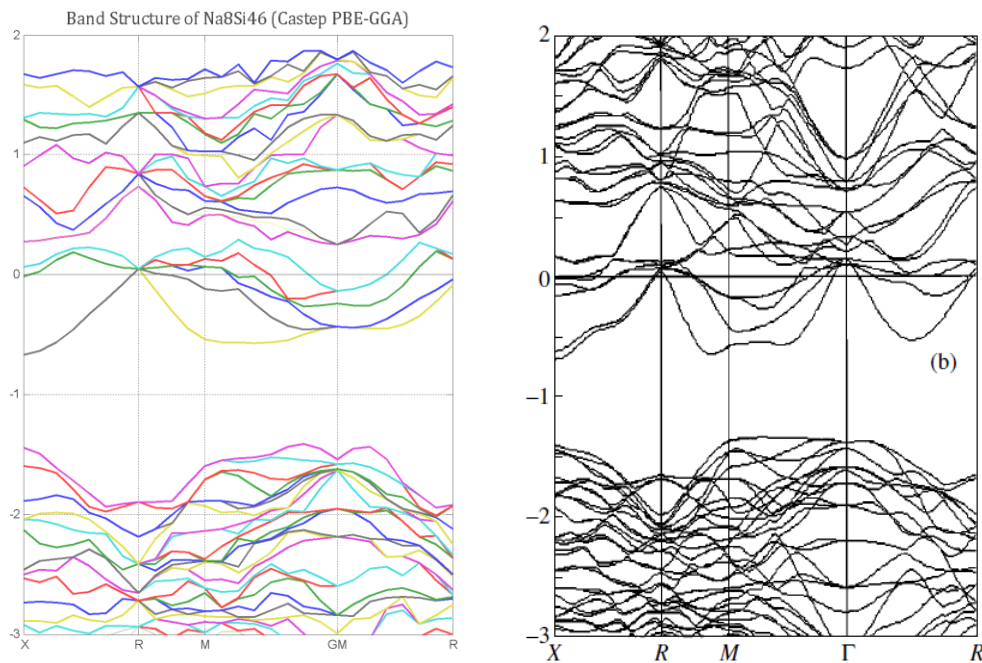
Table n°2: Crystallographic data and structural optimization of $\text{Na}_8\text{Si}_{46}$

	Total energy (eV)	Max force / atom (eV/Å)	Atomic positions (Si)	Atomic positions (Na)	Lattice parameters (Å)
Initial [17]	-15370.9870	0.20824	6c: (0 0,310 0,116) 16i: (0,183 0,183 0,183) 24k: (0,25 0 0,5)	0,0 0,0 0,0 0,5 0,0 0,25	10,19
Relaxed	-15371.2477	0.00215	6c: (0 0,3071 0,1176) 16i: (0,18378 0,18378 0,18378) 24k: (0,25 0 0,5)	0,0 0,0 0,0 0,5 0,0 0,25	10,19
Experimental [16]	/	/	6c: (0 0,30981 0,11762) 16i: (0,18483 0,18483 0,18483) 24k: (0,25 0 0,5)	0,0 0,0 0,0 0,5 0,0 0,25	10,2006

Band structure

Figure 4 illustrates the band structure of $\text{Na}_8\text{Si}_{46}$ clathrate, from our calculation using the CASTEP package, with the GGA-PBE pseudopotential method, compared with the result of Kurganskii *et al* [14], obtained by the Full potential Linearized augmented plane wave FP-LAPW method. The comparison shows a fair agreement between both results, a small difference is related to the different methods (Full potential and Pseudopotential).

It's clear from both band structures that the $\text{Na}_8\text{Si}_{46}$ clathrate has a metallic behavior, this can be explained by the presence of Na atoms as dopant, these atoms supplies each one, valence electron, therefor, the Fermi level will be shifted up, and the conduction band will stick to the valence band. A more extensive explanation is indicated in the reference [14].

**Figure.III.5.** Band structure of $\text{Na}_8\text{Si}_{46}$ calculated by GGA-PBE (Castep)

Density of states

Figure shows the total and partial density of states of $\text{Na}_8\text{Si}_{46}$ clathrate.

Analyzing partial DOS, we notice that there is not a strong bonding between guest and host atoms, but small van der Waals interactions, this is due to the small atomic radius of Sodium atoms.

Total DOS is composed by the contribution of Si atoms in the range of $[-12, 4\text{eV}]$, by their (s) and (p) orbitals (partial DOS of Si), which is responsible for the bounding of Si framework atoms, via an SP^3 hybridization, on the other hand we notice two peaks at and respectively for the Sodium atoms (Na partial DOS), this peak comes from the (p) orbital of Na atoms and hence, there exist no interaction between Na and Si atoms, due to the small size of Na atoms.

Electronic density: Figure III.6 below illustrates the calculated electronic density maps of $\text{Na}_8\text{Si}_{46}$ compound, we see clearly that Na atoms due to their small size has almost no interaction between them and the surrounding Si atoms.

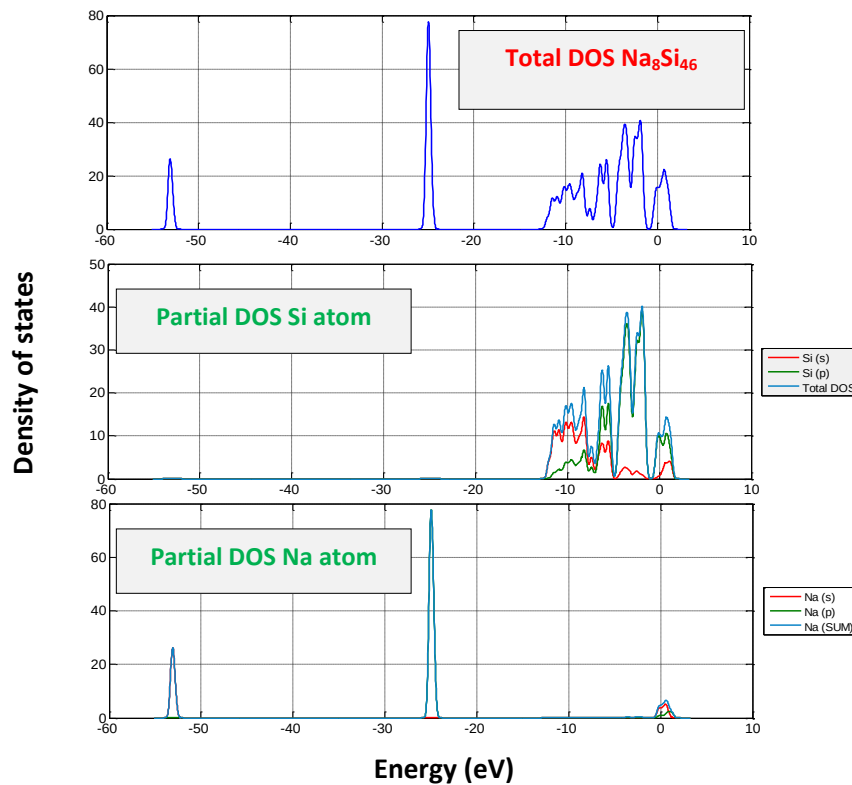


Figure.III.5. Total and partial DOS $\text{Na}_8\text{Si}_{46}$

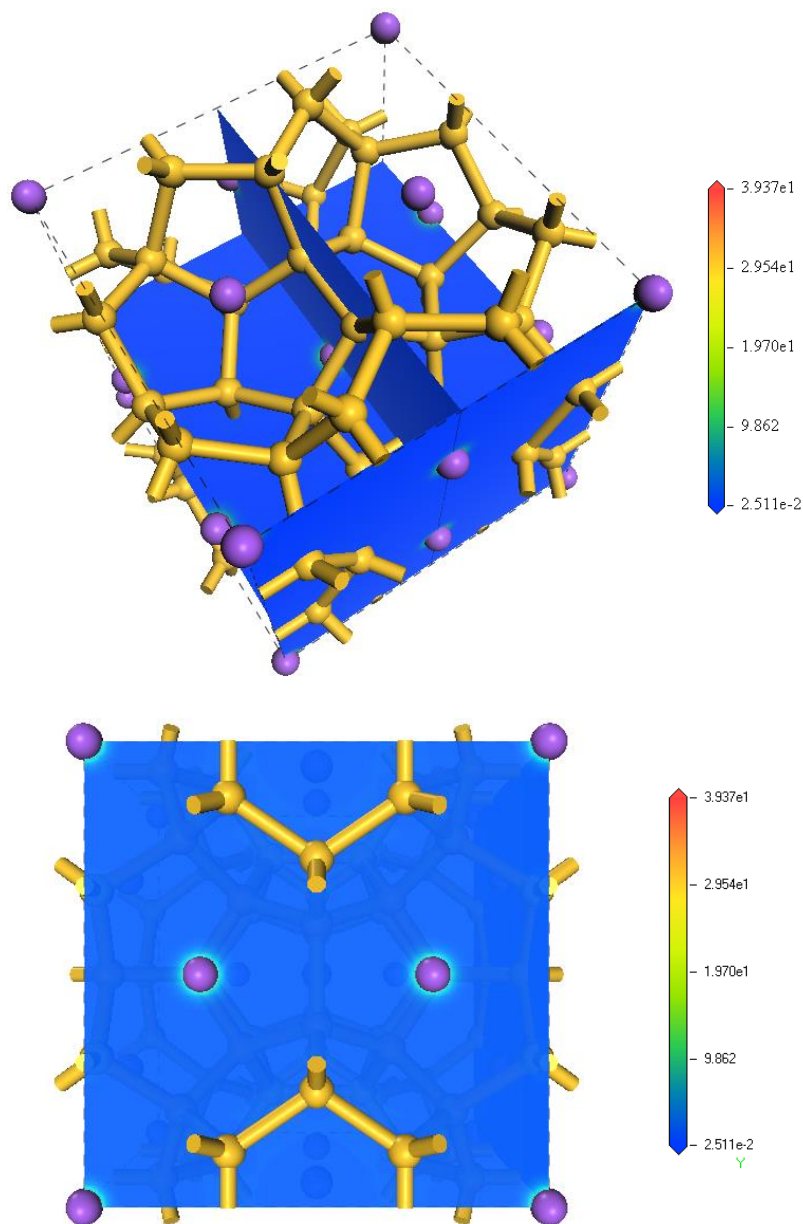


Figure.III.6. Charge density diagram of $\text{Na}_8\text{Si}_{46}$ in $[110]$ plane.

III.6. $\text{Ca}_8\text{Si}_{46}$

The crystalline data of Calcium doped Si clathrate: ' $\text{Ca}_8\text{Si}_{46}$ ' compound, was taken from Reference [17], Firstly, total energy is calculated, and then minimized through geometrical optimization of the system, which was done as second step. The lattice parameters and atomic positions before and after structural relaxation are listed in the table below.

Table n°3: structural optimization of $\text{Ca}_8\text{Si}_{46}$

	Total energy (eV)	Max force / atom (eV/Å)	Atomic positions (Si)	Atomic positions (Ca)	Lattice parameters (Å)
Initial [17]	-12952.8330	0.30403	6c: (0,25 0 0,5) 16i: (0,183 0,183 0,183) 24k: (0 0,310 0,116)	0,0 0,0 0,0 0,25 0,5 0,0	10,230
Relaxed	-15371.2477	0.00215	6c: (0,25 0 0,5) 16i: (0,18378 0,18378 0,18378) 24k: (0 0,3071 0,1176)	0,0 0,0 0,0 0,25 0,5 0,0	10,230

III.6.1-Band structure

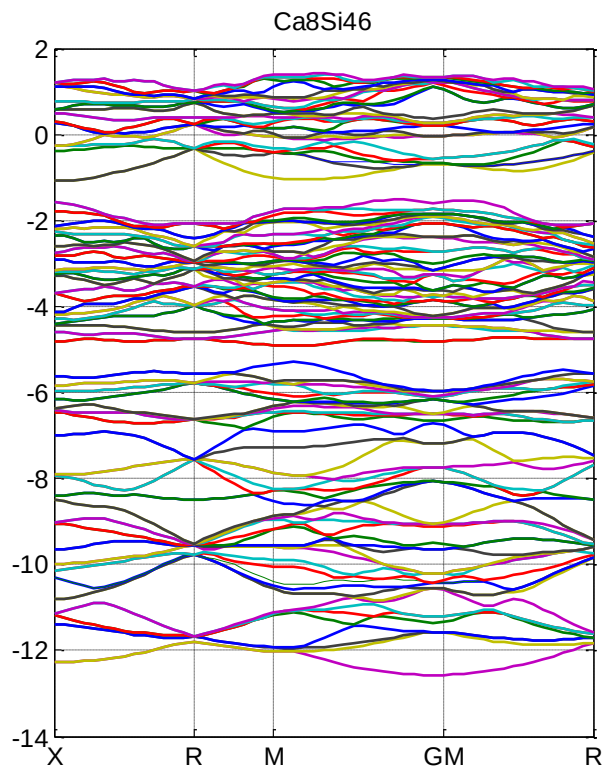


Figure III.7: $\text{Ca}_8\text{Si}_{46}$ calculated band structure

III.6.2- Density of states

The total density of states, comes from contribution of both silicon and calcium atoms, from partial DOS of Si, its sub-total DOS is related to peaks from s and p orbital “sp³ hybridization” which confirm the Si-Si bonding. While partial DOS of Ca atoms, is composed essentially by d orbitals.

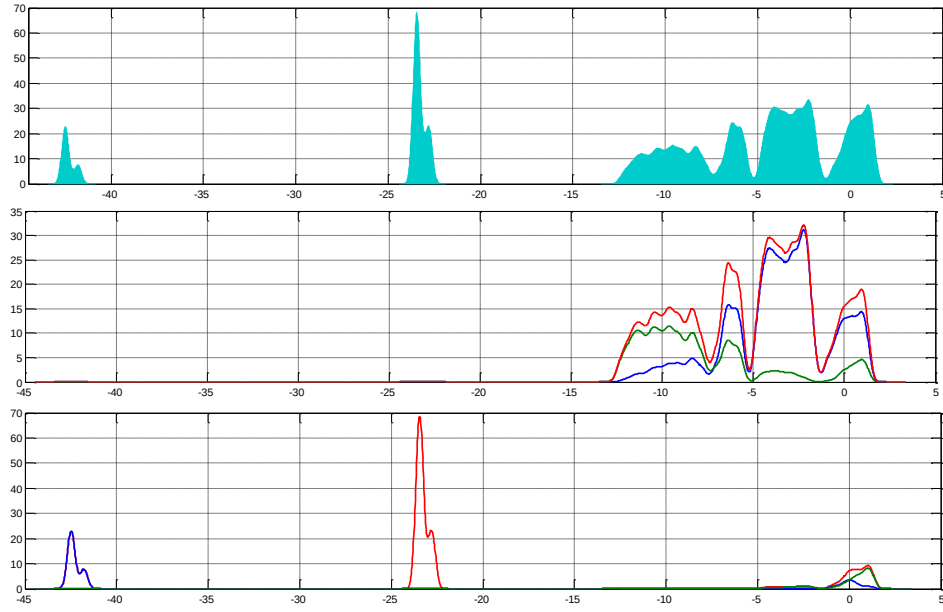


Figure III.8: PDOS and Total DOS of $\text{Ca}_8\text{Si}_{46}$ (GGA-PBE)

III.7. $\text{Ba}_8\text{Si}_{46}$

Barium doped clathrates are the most studied and investigated compounds among all type I clathrates, these compound has revealed during past decades amazing thermoelectric and superconducting properties.

The fourth compound in this work is the Barium doped Si-clathrate $\text{Ba}_8\text{Si}_{46}$, like the previous calculations, we extracted lattice parameters and atomic position from literature, Ref [2], we need to relax the structure to get the minimal total energy; the results of this operation are detailed in the table4:

Table n°4: structural optimization of $\text{Ba}_8\text{Si}_{46}$

	Total energy (eV)	Max force / atom (eV/Å)	Atomic positions (Si)	Atomic positions (Ba)	Lattice parameters (Å)
Initial	-12952.8330	0.30403	6c: (0,25 0 0,5) 16i: (0,183 0,183 0,183) 24k: (0 0,310 0,116)	0,0 0,0 0,0 0,25 0,5 0,0	10,3141
Relaxed	-15371.2477	0.00215	6c: (0,25 0 0,5) 16i: (0,18378 0,18378 0,18378) 24k: (0 0,3071 0,1176)	0,0 0,0 0,0 0,25 0,5 0,0	10,3141

After that we calculate electronic properties of this compound.

Band structure

As the two later compounds, Barium atom will add extra electrons from its valence state to the conduction band of Si. This will shift up the Fermi level and gives the metallic behavior to the structure. The band structure of $\text{Ba}_8\text{Si}_{46}$ is shown in figure III.9.

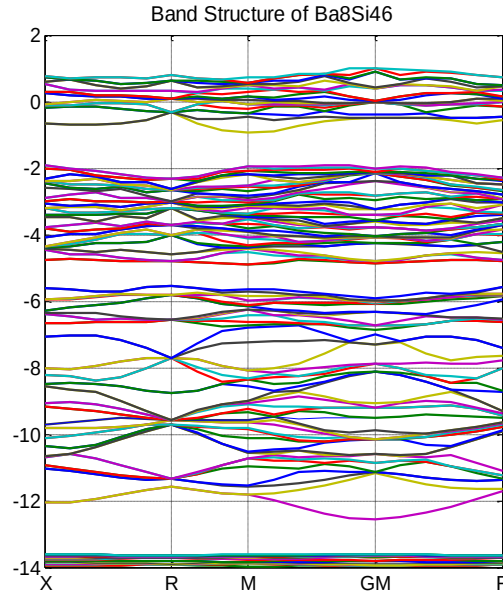


Figure III.9: Electronic band structure of $\text{Ba}_8\text{Si}_{46}$ (GGA-PBE)

III.8. K_8Si_{46}

We study the Potassium doped Si-clathrate. Structural parameters were taken from Ref [2]. Table 5 presents details about atomic positions and lattice parameters before and after geometrical optimization.

Table n°5: structural optimization of K_8Si_{46}

	Total energy (eV)	Max force / atom (eV/Å)	Atomic positions (Si)	Atomic positions (Ba)	Lattice parameters (Å)
Initial	-11172.6299	0.03566	6c: (0,25 0 0,5) 16i: (0,183 0,183 0,183) 24k: (0 0,306 0,1186)	0,0 0,0 0,0 0,25 0,5 0,0	10,30
Relaxed	-11172.7920	0.00002	6c: (0,25 0 0,5) 16i: (0,185 0,185 0,185) 24k: (0 0,307 0,1188)	0,0 0,0 0,0 0,25 0,5 0,0	10,27518

After getting optimized structure for our compound, we carried out calculation of its electronic properties.

III.8.1. Band structure

The calculated band structure is shown in the figure III.10, as precedent compounds, this material shows metallic behavior. So far we have noticed that there is a similarity between band structures of our materials, even changing host atom specie does not affect the band structure allure, but only change its distribution, this, in fact, is a well-known properties and can be taken as a feature in clathrate materials of the same type (I or II), and mentioned in the literature as the ‘rigid band model’. We can see that from our calculations we confirmed this theory.

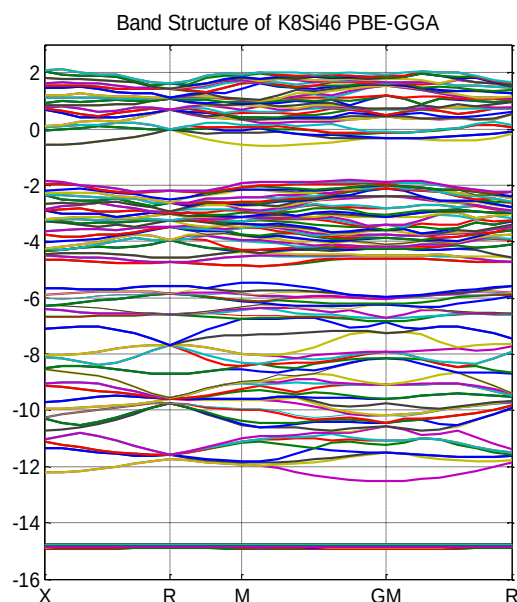


Figure.III.10: Band Structure of K_8Si_{46}

III.8.2. Density of states

We calculated total and partial density of states for K_8Si_{46} clathrate, figure illustrates those densities of states, we also notice in this case that there's a very small ionic interaction between host Si, and guest K atoms even if Potassium atoms are larger than previous ones.

III.9. Rb_8Si_{46}

The last compound in this first study is the Rubidium doped Si-clathrate Rb_8Si_{46} , we had to construct a hypothetical structure because there is not a such structure, due to the size of Rb atoms, these atoms as we see in Fig are the largest among those who are the subject of our investigation, in consequence, only the large cages of Si frame are filled, the small cages will remain empty and

that's why we only found $\text{Rb}_6\text{Si}_{46}$ in the literature. Our calculations of total and partial DOS shows that there is a strong bonding between Rb (guest) and Si (host) atoms, which in reality is impossible.

Structural optimization results are given in table

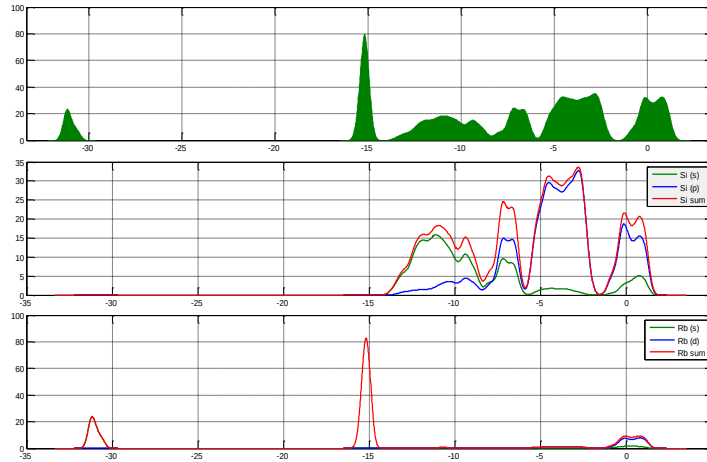
Table n°6: structural optimization of $\text{Rb}_8\text{Si}_{46}$

	Total energy (eV)	Max force / atom (eV/Å)	Atomic positions (Si)	Atomic positions (Ba)	Lattice parameters (Å)
Initial	-11172.6299	0.03566	6c: (0,25 0 0,5) 16i: (0,183 0,183 0,183) 24k: (0 0,306 0,1186)	0,0 0,0 0,0 0,25 0,5 0,0	10,30
Relaxed	-11172.7920	0.00002	6c: (0,25 0 0,5) 16i: (0,185 0,185 0,185) 24k: (0 0,307 0,1188)	0,0 0,0 0,0 0,25 0,5 0,0	10,27518

From these optimized parameters, we launch electronic structural properties calculations.

III.9.1. Density of states

We calculated total and partial density of states of $\text{Rb}_8\text{Si}_{46}$. It is important to notice from figure 17, that the density peak of rubidium atom is getting closer to the density of silicon atom, which means that the interaction between both (guests and hosts) is becoming stronger, due to the large size of Rb atoms. We remind that this structure is hypothetical and generated from experimental $\text{Rb}_{6.5}\text{Si}_{46}$ available in the literature [18]. For more clearance, charge density map is plotted in figure 18 below.



III.9.2. **Figure III.11: Total and partial density of states of $\text{Rb}_8\text{Si}_{46}$**

Charge

density

From charge density diagram, we see clearly that the interaction host-guest showed above in density of state plots, is due to the size of guest atoms, these atoms are large enough to induce stronger ionic

bonding. In fact Rubidium atoms only occupy Si_{24} large cages, the other S_{20} cages remain empty and we found the chemical formula $\text{Rb}_6\text{Si}_{46}$, as investigated in the reference [18].

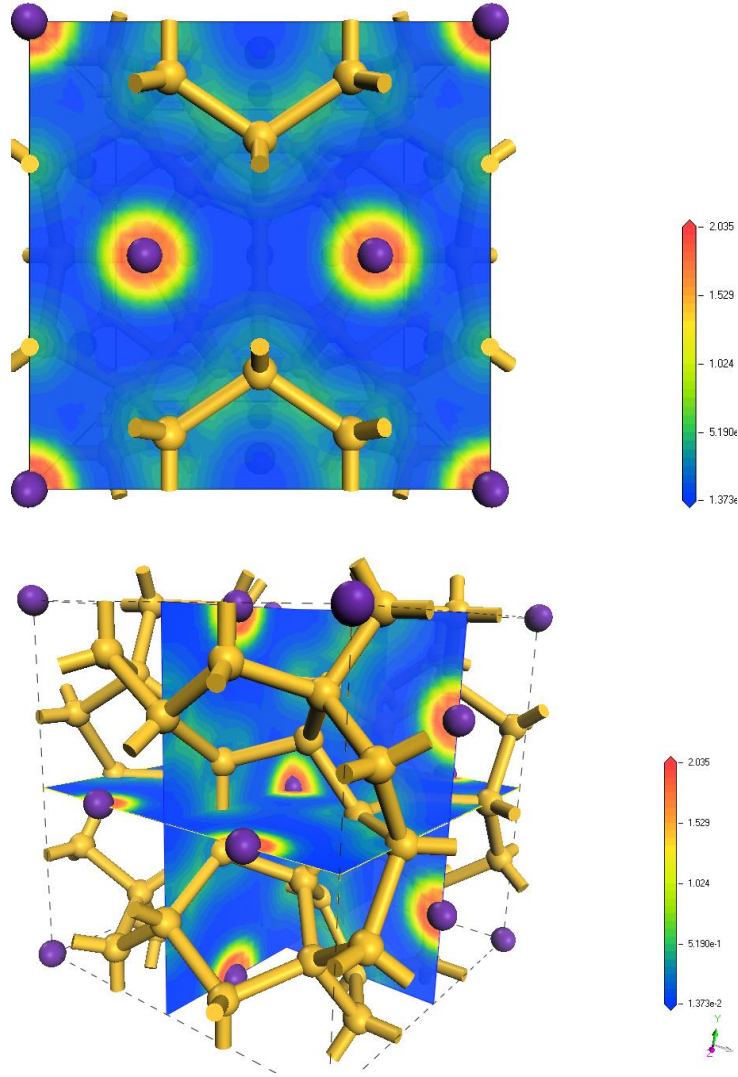


Figure III.12: Charge density diagram of $\text{Rb}_8\text{Si}_{46}$ in the [110]

III.10. Conclusion

In this chapter, we had three major goals to be achieved. First one is to get familiar with some ab-initio methods and to discover a well-known and reliable ab-initio package CASTEP. Hence, at this step we're getting a good amount of experience and confidence to pass to the next step of work. Second goal was to enter the next stage of the thesis work, by discovering and investigating structures of some clathrate materials that are the subject of the thesis, firstly by analyzing the

literature (papers, thesis ...), and then to have the ability to calculate their physical through the CASTEP tool.

Analyzing our results, we noticed that the enclosed guest atoms within Si frameworks, as they get larger (atomic radius), they don't affect the lattice parameter, this was explained in previous works available in the literature as enhancing factor for hardness and integrity these cage-like materials.

Concerning band structures, we noticed by comparing all results, that for all X_8Si_{46} clathrate, the form and distribution of band structure has similar allures, this was also explained in the literature as obeisance to the 'rigid band model' which in our case was confirmed.

As we go from small atoms to large ones, we noticed that there's a difference in density of states, this difference concerns guest atoms, as they reveal density peaks, the more guest atom is larger, the more its density peak get closer to silicon's one. This certainly explains the appearance of weak ionic bonding between host and guest atoms, and also clarifies the strength and integrity of larger guest clathrates. Next chapters will deal with our published results of DFT calculations and bandgap engineering of type-I and type-VIII clathrates.

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CHAPTER IV

Bandgap engineering of guest-free Silicon clathrate Si₄₆

Abstract

This chapter, which is based mainly on the article: “Prediction of indirect to direct band gap transition under tensile biaxial strain in type-I guest-free silicon clathrate Si₄₆: A first-principles approach”, exhibits the results of the bandgap engineering of silicon clathrate Si₄₆. We suggest a bandgap engineering approach of first-principles calculations on basis of density functional theory (DFT), to monitor the bandgap transition from indirect to direct for the type-I guest-free silicon clathrate (Si₄₆). Hence, we have systematically investigated the effect of planar biaxial strain in either compressive or tensile directions on electronic and optical properties using both GGA-PBE and hybrid GGA-BLYP functionals as implemented in Castep and Dmol³ codes respectively. For unstrained Si₄₆, electronic structure has revealed a semiconducting behavior with quasi-direct bandgap estimated at 1.364eV (GGA-PBE) and 1.618eV (GGA-BLYP). Thus, we predict that tensile biaxial strain above +2% can trigger the indirect to direct bandgap transition, which will be located at the X(1/2,0,0) high symmetry point in the first Brillouin zone. The bandgap magnitude increases with the decreasing of biaxial strain and reaches a maximum value of 1.406eV (GGA-PBE) and 1.641eV (GGA-BLYP) at +1% tensile strain, and starts to decrease toward smaller values when the strain is increased. In addition, some relevant optical properties such as the complex dielectric function and the absorption coefficient are computed at each step of biaxial strain. Under tensile strain of +4%, results show better optical properties, the general magnitude of the absorption spectrum is increased by 17.5% with a maximum magnitude of 2.7×10^4 in the visible range of the electromagnetic spectrum.

IV.1. Introduction

Beside its leading status as key material in microelectronics and optoelectronics, silicon thrones the photovoltaic market by a dominative share. This leading position is actually due to its many advantages, it is the second most abundant substance on the earth's crust after oxygen (presenting about 25.8% earth's global mass), it has a very stable and excellent oxide SiO₂ [1], its physical-chemical properties are well established and mastered at both research and industrial levels. However, its development as a strategic material for photovoltaics is permanently challenged by its

shortage related to the indirect nature of its bandgap, which means that an excited electron in valence band requires a change in its momentum to leap to conduction band by an intervention of a phonon in the bulk. In consequence, this makes silicon a very weak light absorber, the thickness of the absorber layer must be at least equal or superior to the mean-free path of charge carriers to skip the recombination phenomena in the bulk, making the first-generation solar cells of silicon relatively thick (about 200 μm) [2]. In order to overcome this problem, the research society came with many innovative and diverse solutions, such as predicting semiconductors with direct bandgaps, as for the case of III-V (GaAs) [3], Chalcopyrites CIGS [4] and cadmium telluride CdTe [5] which already have revealed promising high efficiencies. So far the wide development and mass production of these materials is limited as they use expensive and rare precursor elements such as indium, gallium, and sometimes toxic as arsenic, selenium and cadmium. An ideal solution would be to keep silicon as the main material, and try to engineer its atomic structure to get desired properties [6]. In this context, other allotropic forms of silicon are explored and have exhibited promising physical-chemical properties that could be used in energy conversion systems. Depending on their atomic arrangement and their method of synthesis different forms of silicon-based compounds are obtained. The second known crystalline form after diamond is the cage-like structures named ‘Clathrate’. Clathrates are crystalline inclusion compounds in which the cage formed by host atoms (group IV: C, Si, Ge) encloses within guest atoms or molecules (mostly alkali metal, rare earth or alkaline atoms), [7]. Inspired from hydrate clathrates, their main framework structure consists of face-sharing polyhedrons whose are directly responsible for defining the clathrate’s type. Since their synthetize in 1965 by two French groups Kasper et al [8] and Cros et al [9], group-IV clathrates due to their exceptional thermoelectric [10, 11] and superconductive [12, 13] properties, have encountered a great amount of experimental and theoretical investigations. Recently, this class of material has attracted more attention as candidate for photovoltaic applications, [6, 14]. Type-I Silicon clathrate with chemical formula X_8Si_{46} where X is the guest atom, is the most studied clathrate among the other types, its properties are under investigations and are still revealing more new features, it has been synthetized through a diversity of technics such as arc-melting [15] or high pressure high temperature synthesis HPHT [16, 17]. More recently, thin film based on clathrates including sodium doped silicon clathrates in type-I $\text{Na}_8\text{Si}_{46}$ and type-II $\text{Na}_x\text{Si}_{138}$ [18]. Germanium-gallium clathrates with the chemical formula of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ are successfully grown [19]. An attempt to grow a guest-free Si_{46} silicon clathrate was reported [20], and lately a successful growth of thin film of 1 μm of type-II guest free silicon clathrate Si_{136} over a

(111) Si substrate by thermal decomposition of NaSi precursor films and Na removal from the $\text{Na}_x\text{Si}_{136}$ film by a heat treatment with iodine [21].

In the present study, we aim to establish conditions to obtain direct bandgap silicon that can be useful to achieve better efficiencies for solar cells. To the best of our knowledge, strain technology is a well-known and practical technique used to engineer bandgap of semiconductors, it has been applied to improve performances of structures and devices based on diamond silicon [22-24], however, this technique has not been yet used to tune silicon clathrates properties. With this motivation, we have systematically investigated the impact of the in-plane compressive and tensile biaxial strains on the structural, electronic and optical properties of hypothetical guest-free type-I silicon clathrate Si_{46} by means of first-principles calculation within the DFT approach.

IV.2. Theoretical approach

IV.2.1. Computational details

In this work, our first-principles calculations based on the density functional theory DFT [25, 26] are carried out by CASTEP (Cambridge Serial Total Energy Package) [27] and Dmol³ [28] codes. In order to solve the Kohn-Sham equations of the DFT, Ultrasoft pseudopotentials of Vanderbilt-model included in the Castep package were employed in real space [29]. The exchange and correlation energy (XC) was treated within generalized gradient approximation (GGA) using the Perdew-Burke-Erzenhof PBE parameterization [30], this choice is justified by the fact that GGA-PBE functionals has revealed better convergence of the total energy, the ionization energy and the Si-Si bonds lengths and angles for silicon based compounds compared with the local density approximation (LDA) [31]. By means of a self-consistent-field (SCF) calculations, under criterion for the convergence of the total energy of $5 \cdot 10^{-4}$ eV/atom and 0.001Gpa for pressure, the plane-wave cutoff-energy was set to 480eV, while the first irreducible Brillouin zone in the reciprocal space was sampled at a 6x6x6 grid using the Monkhorst-Pack scheme [32]. In order to minimize the total energy of the system, geometrical and internal coordinates were rigorously relaxed until obtaining ‘Hellmann–Feynman’ interatomic forces lower than 10^{-3} eV/Å, this task was accomplished using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) optimization algorithm [33-36]. For the relaxed configuration, major optical properties were computed for each step of biaxial strain. However, for the calculation of the optical spectra of the dielectric function a dense set of k-points sampling in the Brillouin zone are adopted using 14x14x14 grid of Monkhorst-Pack scheme, which is highly recommended for calculation of optical properties [37]. Hybrid GGA-BLYP [38, 39] functional was

solicited through Dmol³ code [28] to recalculate band structures for optimized structures in order to improve bandgap magnitudes as they are expected to be underestimated by regular GGA-PBE functional. For that purpose, the Brillouin zone was sampled into a grid of 10x10x10 using Monkhorst scheme giving 75 k-points.

IV.2.2. Structural Aspects

Type-I guest-free silicon clathrate Si₄₆ crystallize in the simple cubic space group Pm-3n (number 223) [40]. Its unit cell contains 46 atoms, is formed by assembly of eight face-shared elemental cages: two dodecahedral Si₂₀ (twelve pentagonal faces with 20 atoms) and six tetrakaidecahedral cages Si₂₄ (twelve pentagonal faces and two hexagonal faces with 24 atoms) [40, 41], the vacant cavities within the cages are often filled with guest atoms or molecules. In the present study, the initial lattice is built from crystalline parameters taken from reference [42] ($a=10.055\text{\AA}$), then optimized along with internal atomic coordinates to reach the equilibrium state. At minimum of total energy and interatomic forces, our optimal internal atomic coordinates (following the Wyckoff notation) and lattice parameters are in a good agreement with previous HF-LCCO [43], LDA [44, 45], GGA [46], TBTEMD[42], GTBMD[47] and LDA[48] calculations. Table 1 summarizes our results in comparison with the literature. Figure.1(a) shows a unit cell of X₈Si₄₆ including the Wyckoff positions. Figure.1(b) illustrates the two initial polyhedrons forming the Si₄₆ main framework of the lattice. To the best of our knowledge, experimental values for guest-free type-I Si₄₆ are not reported so far, therefore, we took experimental values of Na₈Si₄₆ as a reference structure [49] ($a=10.19\text{\AA}$) to be compared with. This choice is justified as that due to relative large size of silicon frame-work cages, which is less affected by the presence of guest Na atom where the small atomic radius of Na induces no volume increase in the structural transition between Si₄₆ and Na₈Si₄₆ lattices according to [44]. As regard to the mechanical properties, the cubic nature of clathrate leads to define only three independent elastic constants which are given for type-I clathrate Si₄₆ as: $C_{11}=155,140,135\text{ GPa}$, $C_{12}=65,47,58\text{ GPa}$, and $C_{44}=45,47,40\text{ GPa}$, the density is $\rho=2.1, 2.098, 2.05\text{ g/cm}^3$ as all respectively reported by [42, 50, 51]. We report a density of $\rho= 2.01\text{g/cm}^3$.

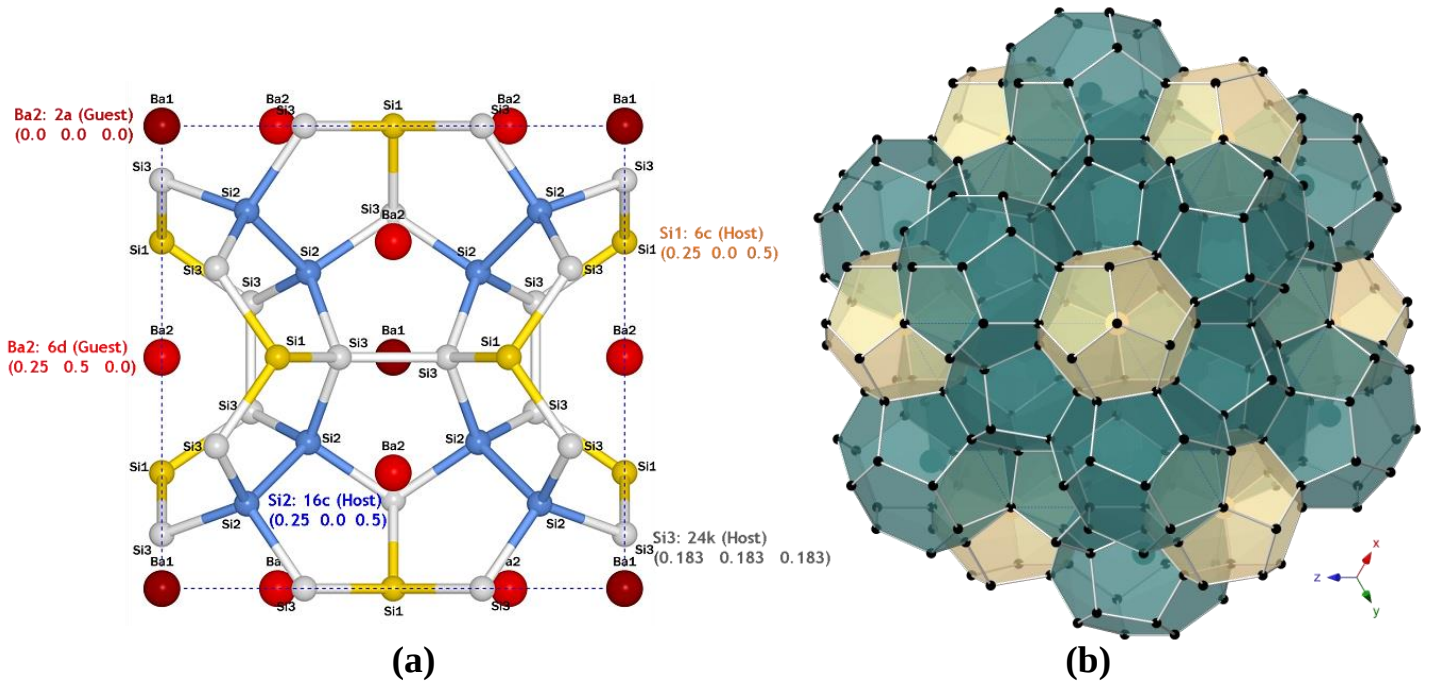


FIG.1: Aspect of the crystalline structure of type-I Silicon clathrate X_8Si_{46} , (space group: $\text{Pm}\bar{3}\text{n}$, No 223). (a) A unit cell of $\text{Ba}_8\text{Si}_{46}$ containing 46 Si atoms occupying the following positions according to the Wyckoff notation: Si1(6c) (yellow), Si2(16i) (gray), Si3(24k) (blue), (6d and 2a) (dark and light red) are occupied by eight Ba guest atoms. (b) Two types of polyhedrons (Si₂₀ (yellow) + Si₂₄ (green)) forming the type-I X_8Si_{46} clathrate framework with guest atoms inside (view down the (111) direction).

Table.I: Optimized lattice parameters and atomic positions of type-I guest-free silicon clathrate Si_{46} (space group $\text{Pm}\bar{3}\text{n}$ (223)) using the GGA-PBE approximation.

	Lattice parameter $a_0(\text{\AA})$							
	10.22 ^a	10.406 ^b	10.19 ^c	10.069 ^d	10.229 ^e	10.055 ^f	10.20 ^g	10.069 ^h
Atom	Site: Wyckoff notation		X		Y	Z		
Si(1)	$6c\ (x, y, z)$		0.25 ^{a,b,c,f}		0 ^{a,b,c,f}	0.5 ^{a,b,c,f}		
Si(2)	$16i\ (x, x, x)$		0.1836 ^a 0.1839 ^b 0.1835 ^c 0.1840 ^d		0.1836 ^a 0.1839 ^b 0.1835 ^c 0.1840 ^d	0.1836 ^a 0.1839 ^b 0.1835 ^c 0.1840 ^d		
Si(3)	$24k\ (0, y, z)$		0 ^{a,b,c,d}		0.3079 ^a 0.3070 ^b 0.3077 ^c 0.3080 ^d	0.1170 ^a 0.1176 ^b 0.1174 ^c 0.1170 ^d		
a: This work (GGA-PBE) b: Data from reference [43] (HF-LCCO: Hartree-Fock linear combination of crystalline orbitals) c: Data from reference [44] (LDA: Local density approximation) d: Data from reference [45] (LAPW: Linearized augmented Plane Wave-LDA) e: Data from reference [46] (GGA-PBE) f: Data from reference [42] (TBTEMD: Tight binding total energy molecular dynamics) g: Data from reference [47] (GTBMD: Generalized tight-binding molecular dynamics) h: Data from reference [52] (LDA)								

IV.3. Biaxial strain simulation

The biaxial strain is applied by imposing a biaxial stress tensor ($\sigma_{11}=\sigma_{22}\neq\sigma_{33}$) on the material where the same amount of stress is applied along the $\langle 100 \rangle$ and $\langle 010 \rangle$ directions $\sigma_{11}=\sigma_{22}\neq 0$ and the out-of-plane axis along $\langle 001 \rangle$ direction is free of stress $\sigma_{33}=0$. The strain tensor can be determined through the Hooke's laws of general elasticity [53-55].

$$(\sigma_{ij})=(C_{ij}) (\varepsilon_{ij}) , i,j=1,2,3 \quad (1)$$

In order to simulate both compressive ($\varepsilon_{11}=\varepsilon_{22}<0$) and tensile ($\varepsilon_{11}=\varepsilon_{22}>0$) in-plane biaxial strains that any epitaxial thin film undergoes when it is grown over substrates with different lattice constants, the lattice parameters at the equilibrium state are modified according to the formulas (2) and (3),

$$\varepsilon_{11} = \varepsilon_{22} = \frac{a - a_0}{a_0} = \frac{\Delta a}{a_0} \quad (2)$$

$$\varepsilon_{33} = \frac{c - c_0}{c_0} = \frac{\Delta c}{c_0} \quad (3)$$

Where: ($\varepsilon_{11}(\%) = \varepsilon_{22}(\%)$) rate correspond to the simulated compressive ($\varepsilon_{11}<0$) and tensile ($\varepsilon_{11}>0$) planar biaxial strains along x- and y-axis respectively, whereas $\varepsilon_{33}(\%)$, presents the induced out-of-plane deformation rate due to the relative displacement along the z-axis. ($a_0=b_0$) are the optimized equilibrium lattice constants, while ($a=b$) represent the new lattice parameters induced from the strained structure of Si_{46} .

The formulas (2) and (3) are often used to model the lattice mismatch between an epitaxial grown thin film on a given substrate, which imposes its lattice parameters on the epitaxial film, consequently induces internal strain. For the obtained stable structure in-plane lattice parameters a and b are calculated and fixed at the values corresponding to a desired strain rate, while the out-of-plane lattice parameter c is relaxed along with the internal atomic coordinates of the strained lattice using the BFGS optimization algorithm [33-36], keeping same criterions as described in the computational procedures section. Calculations including strain between -4% (compressive) to +4% (tensile) by steps of 1% were considered.

IV.4. Results and discussion

IV.4.1. Electronic properties of unstrained Si₄₆

Figure.2 depicts the calculated band structure with (a) GGA-PBE and (b) GGA-BLYP. In both figures the path of k-vector in the first Brillouin zone is chosen to follow the X-R-M- Γ -R high symmetry segments, and the Fermi energy is set to the zero energy reference. According to the chosen Ultrasoft pseudopotentials in GGA-PBE, each silicon atom is modeled using the following electronic configuration Si:[Ne] 3s² 3p² as given in [29], where 92 valence bands were considered. We have chosen 20 empty bands for setting the conduction bands in both cases. For the unstrained state, Si₄₆ exhibits an indirect bandgap with semiconductor feature, where the valence band maximum (VBM) appears between M(1/2,1/2,0) and Γ (0,0,0) segment, whereas, the conduction band minimum (CBM) lies at the X(1/2,0,0) point. The band structure of Si₄₆ was investigated from theoretical point of view. So far, no experimental data is reported due to the difficulty of obtaining a guest free type-I Si₄₆ cages where silicon stabilize under diamond structure during synthesis. For the present calculated band structure, comparison with guest-containing clathrates (such as Na₈Si₄₆) is possible since all type-I clathrates obey the rigid-band model, which means that all those compounds will have similar allures of band structures and differ only in the Fermi level position and the bandgap magnitude, which is affected by the type of the guest atom [45]. In this work we report a quasi-direct band gap equal to E_g=1.364eV (GGA-PBE) and E_g=1.618eV (GGA-BLYP). It is well-known that the ground state DFT calculations have a tendency to underestimate the bandgap [56], however, our results are in fair agreement with previous theoretical data: E_g= 1.26eV [40], 0.9eV [45], and 1.315eV [57]. As illustrated in figure.2(a) and 2(b), band structures of unstrained Si₄₆ indicate that the valence band is subdivided to two major regions counting each 46 band: the lower valence band (LVB) between -11eV and -4eV, which is mainly formed by a large electronic contribution of the 3s- and small contribution of 3p-states of Si atoms. Whereas, the upper valence band (UVB between -3eV to 0eV) is formed by a large contribution from 3p-states and a very small contribution from 3s-states. The conduction band (CB) is dominated by the 3p-states of silicon atoms. Total and partial density of states DOS plot illustrated in figure.3, were also computed using regular GGA-PBE and hybrid GGA-BLYP functionals. Figure.3(a) (GGA-PBE) indicates that the Si-Si bonding within the system is covalent and comes from the contribution of 3p² and 3s² states forming strong (sp³) hybridization, in agreement with the common electronic features of silicon based structures. Thus, figure.3(b) (GGA-BLYP) shows similar allure of total DOS and an extra electronic contribution from Si-d orbitals.

IV.4.2. Electronic properties under biaxial strain

In order to investigate the effect of the applied planar biaxial-strain on the electronic properties of Si_{46} clathrate, electronic band structures were computed for each step of tensile and compressive biaxial strains ranging from -4% to +4%. The calculated bandgap magnitude versus biaxial-strain is illustrated in Figure.4. Under biaxial strain, magnitude of bandgap changes significantly where a maximum value $E_g=1.406\text{eV}$ (GGA-PBE) and 1.641eV (GGA-BLYP) is reached at tensile strain of +1%. It starts then to decrease for higher tensile strains, whereas, for compressive strains below 0%, it decreases significantly until reaching its minimum value of $E_g=0.895\text{eV}$ (GGA-PBE) and 1.112eV (GGA-BLYP) at -4% rate. Figure.5 depicts the electronic band structures for -1% (a), -2% (b), -3% (c), -4% (d) +1% (e), +2%(f), +3%(g) and +4%(h) strained Si_{46} . We notice from these figures that the bandgap nature remains quasi-direct for compressive strains. For $\Delta a/a_0 = -3\%$ and -4% the valence band maximum is located in the $\Gamma(0,0,0)$ -R(0,1/2,1/2) high symmetry segment, and the conduction band minimum remains at the X(1/2,0,0) high symmetry point. For the unstrained and the $\Delta a/a_0 = -1\%$, -2%, +1% states, the VBM will transit to the segment between $\Gamma(0,0,0)$ and M(1/2,1/2,0), the bandgap remains indirect and the CBM still at the X point. For tensile strains equal and superior to +2% the valence band maximum VBM shifts down from its previous position between Γ and R, and appears at the X(1/2,0,0) point to coincide with the CBM leading to transformation of the quasi-direct bandgap into a direct bandgap. For more insight Figure.6 exhibits the influence of the biaxial strain on the higher valence bands of the unstrained and +3% -3% strained Si_{46} . Figure.7 shows the variation of the total density of states DOS as a function of the applied strain, it indicates increasing of the magnitude with decreasing of the strain condition, higher density of states are obtained when the bandgap is direct ($\epsilon_{11}, \epsilon_{22} > +2\%$).

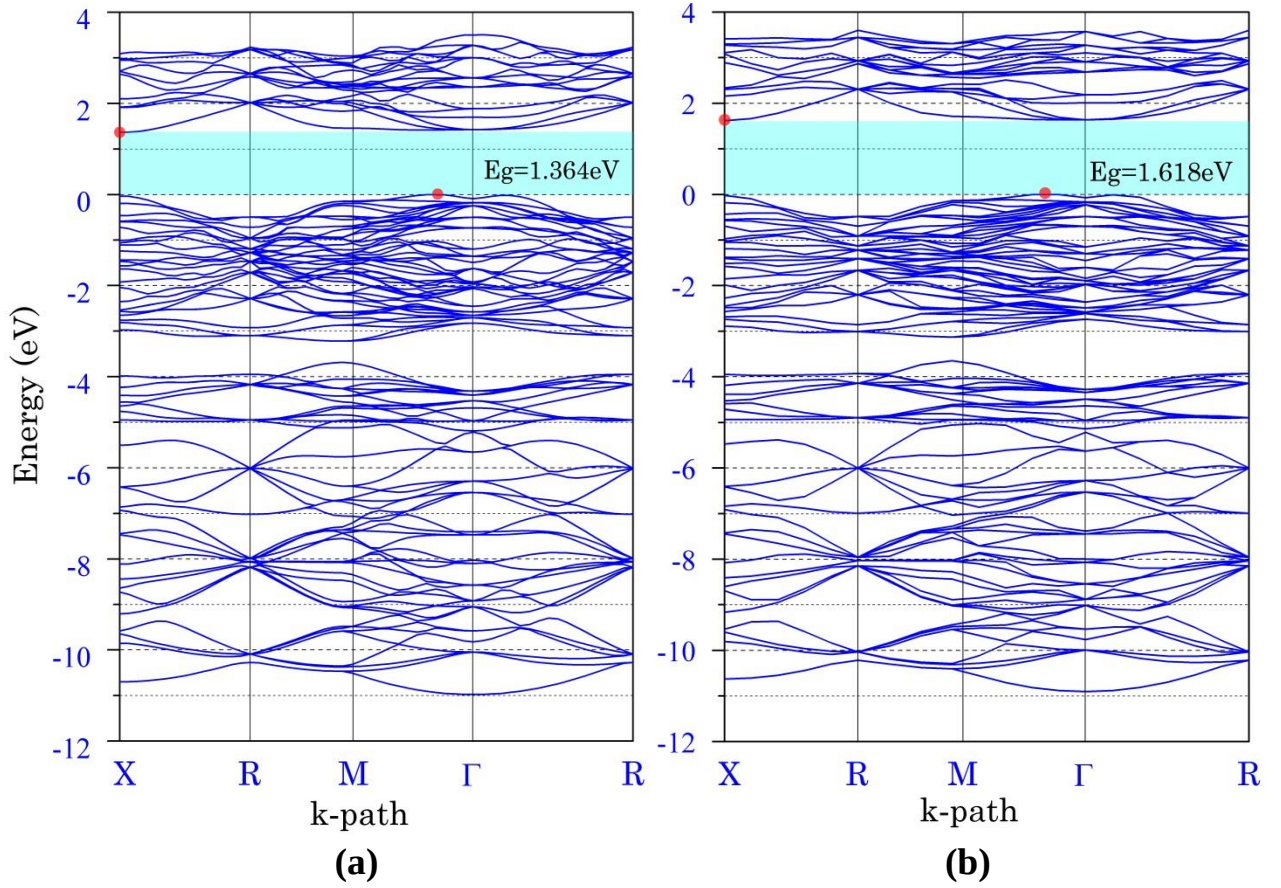


FIG.2: The calculated band structure of unstrained type-I silicon clathrate Si_{46} using (a) GGA-PBE and (b) hybrid GGA-BLYP functionals with Castep and Dmol³ respectively. Valence band maximums VBM and Conduction band minimums CBM are indicated in red dots.

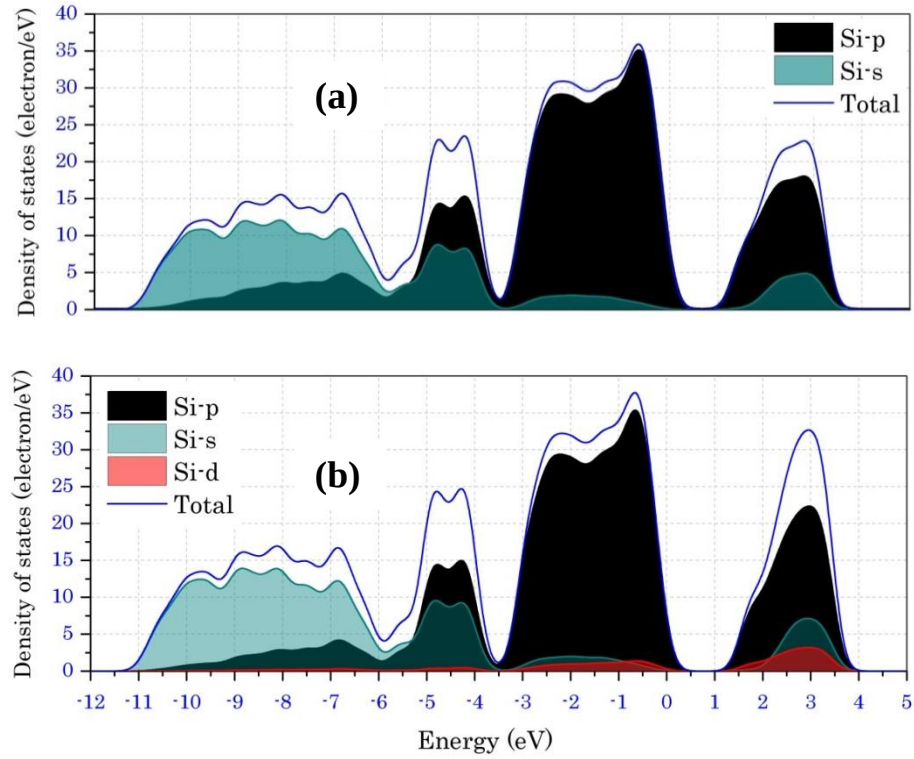


FIG.3: The calculated total and partial density of states for unstrained type-I silicon clathrate Si_{46} using (a) GGA-PBE and (b) hybrid GGA-BLYP functionals with Castep and Dmol³ respectively.

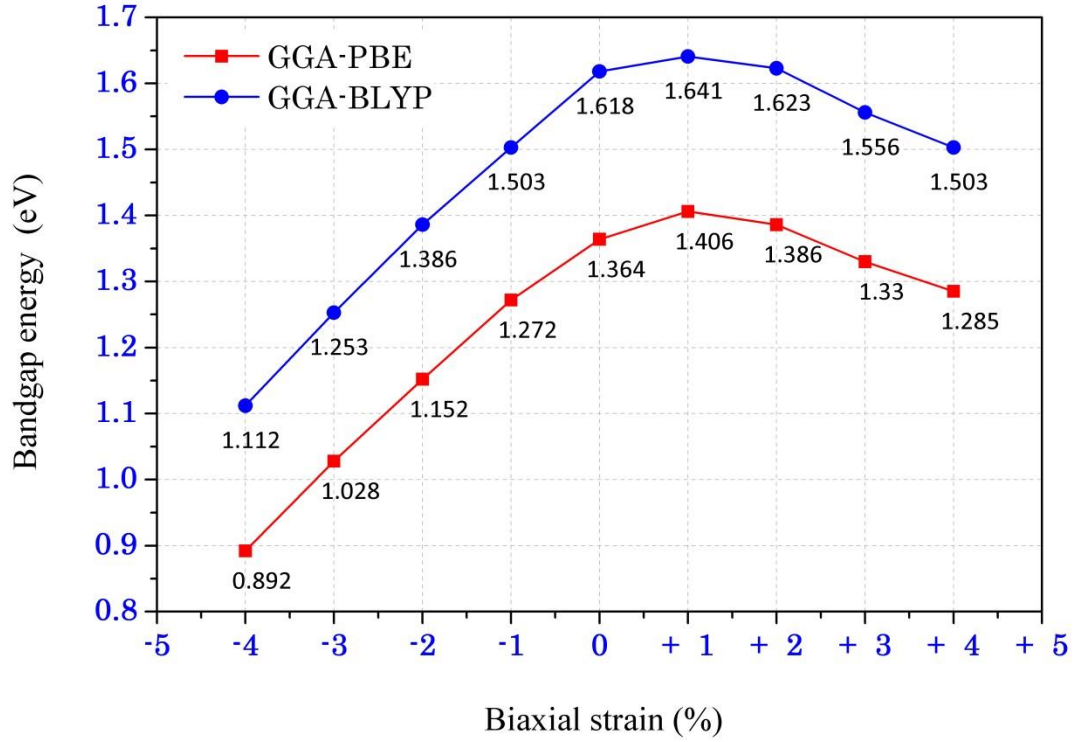


FIG.4: Band gap magnitude as a function of biaxial strain for type-I Si_{46} calculated using GGA-PBE and hybrid GGA-BLYP

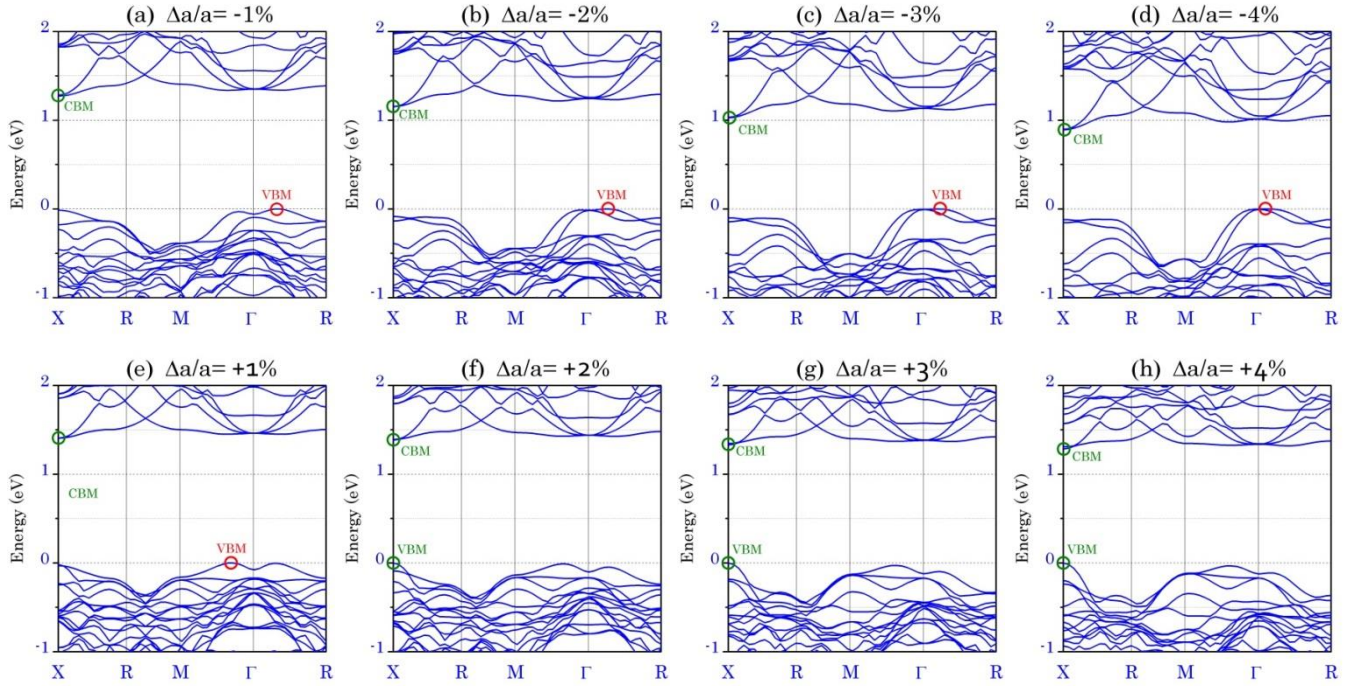


FIG.5: Electronic structures of strained Si_{46} : (a) -1%, (b) -2%, (c) -3%, (d) -4%, (e) +1%, (f) +2%, (g) +3% and (h) +4%. VBM and CBM points are indicated in colored circles. For strains ($> +2\%$) the bandgap is direct @ $X(1/2,0,0)$.

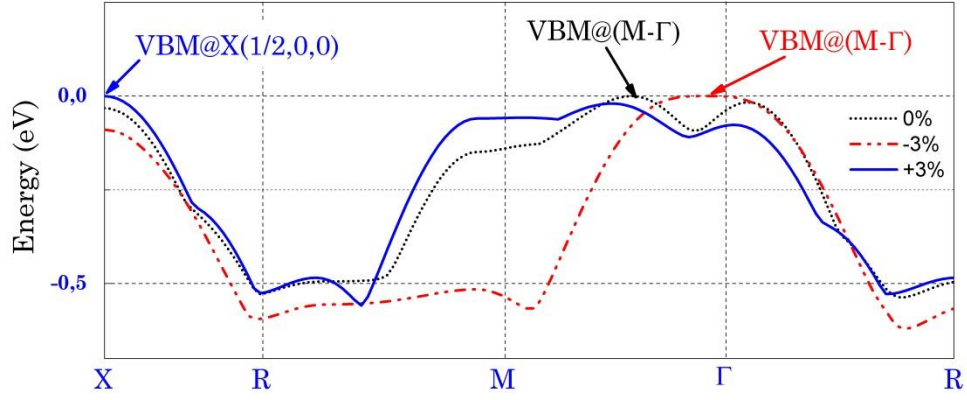


FIG.6: Valence band maximum VBM of Si₄₆ as function of biaxial strain

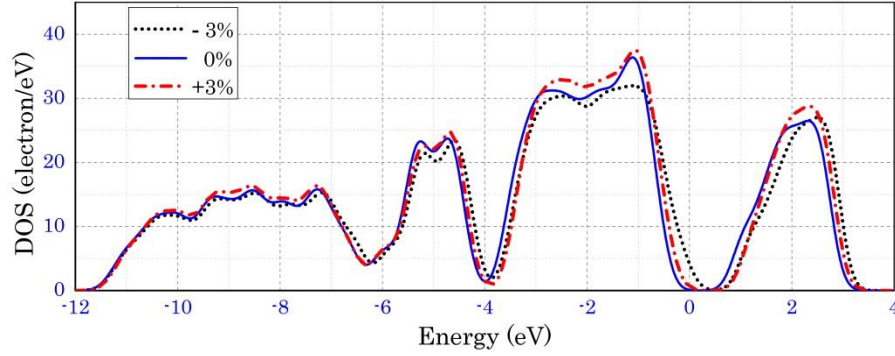


FIG.7: Influence of biaxial strain on the total density of states of type-I Si₄₆.

IV.4.3. Optical properties under biaxial strain

All optical properties of materials are quantified by means of the frequency-dependent complex dielectric function $\varepsilon(\omega)$, expressed as: $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, which represents the linear response of the system to an external electromagnetic excitation [58]. The imaginary part $\varepsilon_2(\omega)$, is computed from the momentum matrix elements taking all possible transitions between the occupied and unoccupied wave functions following the selection rules [59, 60] using the following formula:

$$\varepsilon_2(\omega) = \left(\frac{2e^2\pi^2}{m^2\omega^2} \right) \sum_{ij} \int \langle i | M | j \rangle^2 f_i (1 - f_i) \delta(E_f - E_i - \omega) d^3k \quad (4)$$

Where: i and j are the initial and final states, M represents the dipole matrix, f_i is the Fermi distribution function for the i^{th} state and E_i is the energy of the electron in this state.

The real part $\varepsilon_1(\omega)$ is extracted from the imaginary part through the following Kramers-Kronig formulation [59, 60]:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\omega' \varepsilon_2(\omega') d\omega'}{(\omega'^2 - \omega^2)} \quad (5)$$

From the complex dielectric function, other important optical properties such as absorption coefficient $\alpha(\omega)$ can be extracted. In this context, we have computed using GGA-PBE the complex dielectric function and the absorption coefficient as a function of the incident light energy for each rate of biaxial strain. Figure.8 shows the calculated imaginary and real parts of the complex dielectric function for strained and unstrained Si₄₆ following two different polarizations, i.e. the (001) transversal polarization (parallel to c-axis) and (100) normal polarization (perpendicular to c-axis). The real part of the dielectric function is calculated and illustrated in Figure.8(a) and 8(b) following the (001) and (100) polarizations respectively. Results in Figure.8(a) are clearly enhanced for the -4% compressively-strained Si₄₆, the maximum peak is located at 2.5eV and the minimum is found at 4.5eV energy. Figure.8(b) shows better values for the +4% tensile-strained Si₄₆, and the extreme peaks appear at the same values of energies as precedent, hence, the three plots have similar shapes, and tend towards zero for higher energies. Figure.8(c) displays the imaginary part of the dielectric function calculated through the (001) plan. The -4% compressively-strained Si₄₆ shows the highest magnitude curve and the maximum peak appears at about 3.8eV energy, while the minimum magnitude is obtained for the +4% strained Si₄₆ at 3.2eV, the unstrained Si₄₆ shows a maximum peak at 3.5eV energy. For the imaginary part calculated through a polarization following the (100) plan illustrated in figure.8(d), it can be noticed that the +4% strained Si₄₆ reveals highest magnitude, while the lowest is obtained for the -4% strained state, this improvement is related to the direct nature of the band gap obtained for tensile strains above +3%.

Absorption coefficient is among the most relevant quantities to evaluate if the material of interest appears to be promising for optoelectronics, photonics or photovoltaic applications; it is directly derived from the dielectric complex function through the formula (6) [59]:

$$\alpha(\omega) = \frac{2k\omega}{c\hbar} \quad (6)$$

Where: ω and c represent the incident light frequency and the celerity of the light in vacuum respectively. Figure.9 shows the computed absorption coefficient for -4%, +4% and unstrained Si₄₆ as a function of energy following the (001) polarization plan, it is noticed that for the tensile biaxial strain of +4% in which the bandgap is direct, the absorption is higher than that of the unstrained or compressively-strained Si₄₆. For unstrained Si₄₆, the maximum peak appears at 4.81eV energy, the magnitude of the peaks decrease for the -4% state, while, for the +4% state, the major peak appears

at 4.94eV and the general magnitude of absorption spectrum is increased by 17.5%. This improvement is directly attributed to the direct bandgap at +4%. The magnitude is at the order of 2.7×10^4 in the visible range within the electromagnetic spectrum (1eV to 4eV). It is primordial to report that in spite of optical transitions are expected to be forbidden in this class of materials according to [44, 61], turning the bandgap into direct through biaxial-strain approach might be a solution to overcome this shortage, therefore, this hypothesis needs to be confirmed through further investigations.

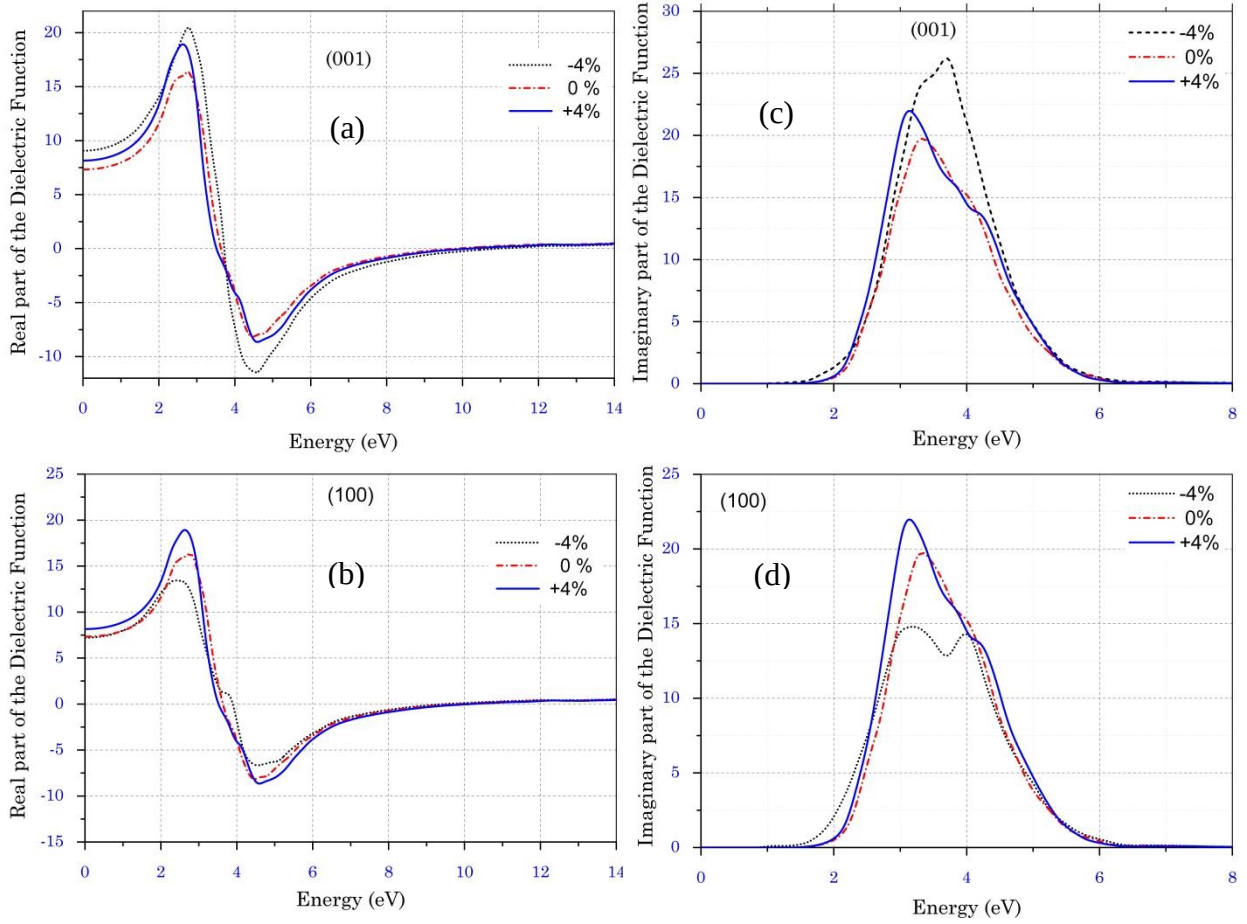


FIG.8: GGA-PBE calculated dielectric function for type-I guest-free Si_{46} , the real part following (a) the (001), and (b) (100) plans, the imaginary part following (c) the (001) and (d) the (100) crystallographic plans

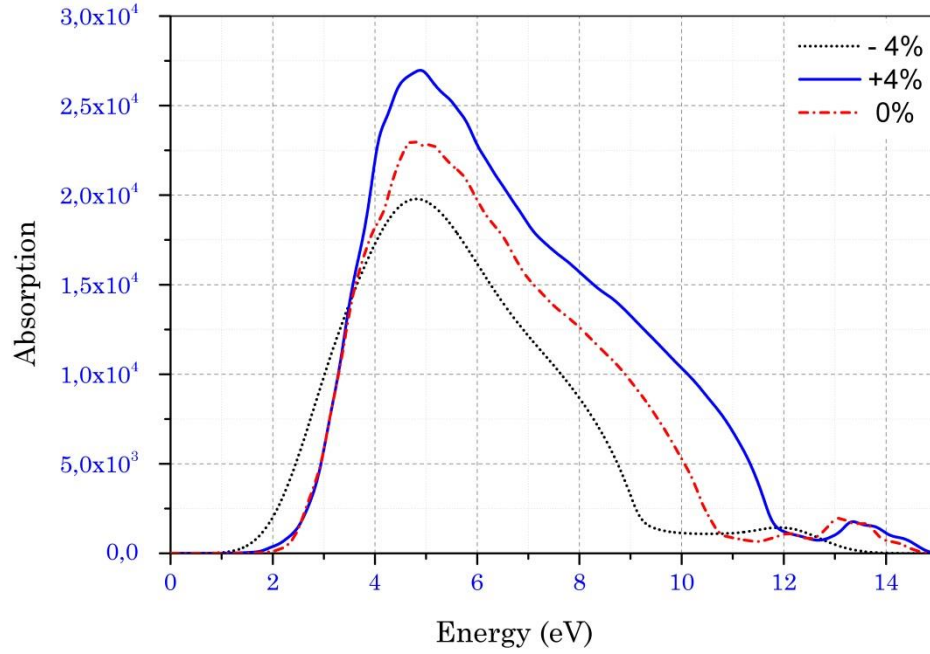


FIG.9: Optical absorption as a function of energy of unstrained and strained Si₄₆ along the (001) c-axis perpendicular plane

IV.5. CONCLUSION

In summary, we have investigated by means of first-principles calculations the effect of planar biaxial-strain on electronic and optical properties of the type-I guest-free silicon clathrate Si₄₆. It was demonstrated that this material could exhibit a direct bandgap under tensile-strains above +2% with magnitudes of 1.381eV (GGA-PBE) or 1.623eV (GGA-BLYP). At this rate, optical properties are clearly enhanced with increasing values for the dielectric function as well as the optical absorption. The tensile biaxial strain of +2% corresponds to a substrate lattice constant of about $a=10.40\text{\AA}$, an adequate substrate to exert this strain can be searched following a systematic study. This finding indicates that the material in question is advantageous for direct bandgap applications such as optoelectronic or photovoltaic devices. We wish this work would provide more perspectives of strain tunability of inorganic clathrates regarding their use in many technological applications and devices.

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CHAPTER V

Comparative investigation of type-I and type-VIII Si₄₆ and their optical properties

Abstract

We systematically study the structural, electronic and optical properties of two types of guest-free Si₄₆ silicon clathrates using first-principles density-functional theory calculations. The properties are compared between two different crystal structures with the same chemical formula of Si₄₆, type-I and type-VIII. We apply hybrid functional approach with Becke, Lee-Yang-Parr (BLYP) functional and compare the electronic properties with those by generalized gradient approximation (GGA-PBE). The band structures of both clathrates calculated within the GGA indicate semiconducting (insulating) properties with the indirect bandgaps of 1.38 and 1.36 eV for the type-I and type-VIII, respectively. These band gaps increase to 1.60 and 1.62 eV by using BLYP hybrid functional. The calculated optical absorption of type-I clathrate is slightly larger than that of type-VIII. Lastly; we also performed a symmetry analysis of optical transitions for both Si₄₆ clathrates. It is found that optical dipole-transitions are allowed at the band-edge located along the Γ -H line for Si₄₆-VIII, while the transitions for type-I Si₄₆ are forbidden by symmetry. It is hoped that this finding will motivate further investigations on the optical capabilities of the all silicon based type-VIII clathrates for photovoltaic and photonic devices.

V.I. Introduction

Photovoltaic and thermoelectric technologies can directly convert light and heat into electricity. Both technologies are of interest as major players in the energy market as the global demand for clean and renewable energy. Therefore, the need for ideal abundant, non-toxic, reusable and robust materials is the motivating factor behind the intensive theoretical and experimental research. Silicon is a scaffolding element of most of the modern high-tech appliances, owing to its abundance, versatility, recyclability, the stability of its oxide SiO₂, and its mature science and industry. Exploration and exploitation of silicon structures beyond the common diamond phase (d-Si) with desired properties that are compatible with the actual silicon-based industries would be a step closer toward cheap and efficient photonic and thermoelectric devices. Clathrates based on silicon were first synthesized in 1965 [1, 2]. It has attracted great attention in the past three decades for their intriguing physical and chemical properties. Silicon clathrates are inclusion compounds wherein

silicon as a “host” material forms a covalently sp^3 bonded cage-like framework entrapping “guest” atoms or molecules with weak van der Waals host-guest interactions [3]. Silicon clathrates are promising candidates for many technological applications such as semiconductor, superconducting [4, 5], optoelectronics [6], thermoelectrics [7, 8], photovoltaics [6, 9, 10], and even regarded as a candidate of electrodes in lithium ion batteries [11]. Among them, silicon clathrates named type-I and II were the most intensively investigated with more than 120 compounds [12, 13].

Recently, type-VIII with the same formula as type-I (X_8Si_{46} , X = guest atom) has emerged as a promising candidate showing high thermoelectric figure-of-merit ZT , owing to their low thermal conductivity [14]. It also shows a large number of electron pockets near the band edges [15]. Quaternary type-VIII silicon clathrates of $Sr_8Al_xGa_{16-x}Si_{30}$ were successfully synthesized. Among them, $Sr_8Al_6Ga_{10}Si_{30}$ has the maximum power factor of $11 \mu Wcm^{-1} K^{-2}$ at 1000 K [16]. Type-VIII clathrates based on tin were also successfully synthesized in single crystals form from Ga and Sn fluxes with both p- and n-type doping [17]. Incorporating copper as a dopant in $Ba_8Ga_{16}Sn_{30}$, it demonstrates the highest values of the figure-of-merit ZT among type-VIII clathrates, where the ZT values of 0.88 and 1.45 at around 500 K, for the p- and n-type crystals respectively [18]. Raman spectroscopy measurements showed that the “guest” vibrational frequencies of type-VIII Si clathrates are higher than those of the type-I. It shows strong guest–host interactions in the clathrates, and it was confirmed that they are best adapted for thermoelectric applications [19]. In this study, we report the electronic and optical properties of type-VIII guest-free Si_{46} clathrates using first-principles density-functional theory (DFT) calculations. The structural features on the electronic and optical properties are compared with those of the type-I clathrates Si_{46} within generalized gradient approximation (GGA). Guest-free silicon clathrates of type-I and VIII are hypothetical structures with promising properties that deserve deeper inspection. Comparison of previous theoretical [20-23] and experimental works [16, 19, 21] shows that both compounds has attractive physical properties with some advantages in the favor of type-VIII clathrate. We also apply hybrid functional approach with Becke, Lee-Yang-Parr (BLYP) functional to compare the electronic properties with those by GGA. The present paper is organized as follows: after the introduction, the second section outlines the theoretical approach including our computational details and the structural aspects of the two clathrates. Section 3 is dedicated to the discussions of the electronic properties and the differences related to the two structural configurations (clathrate type I and VIII). The Optical properties are discussed in detail in the fourth section. Finally, in

section 5 we discuss the optical transitions in both allotropes by means of symmetry-analysis based on group theory.

I. Theoretical approach

II.1. Computational procedures

In the present work, the electronic and optical properties were studied using first-principles calculations based on the density functional theory (DFT) [24, 25] as implemented in CASTEP (Cambridge Serial Total Energy Package) [26] and Dmol³ [27] codes. In the CASTEP code, the Kohn and Sham equations in the DFT framework are solved with ultrasoft pseudopotentials proposed by Vanderbilt [28]. The generalized gradient approximation (GGA) proposed by Perdew-Burke-Erzenhorf (PBE) was used in the exchange and correlation energy (XC) [29]. For silicon based materials, physical properties calculated by GGA are fairly in agreement with experimental values. The values of ionization energy and optimized crystallographic parameters are closer than those by the local density approximations (LDA)[30, 31]. For both types of Si₄₆ clathrates, the self-consistent-field (SCF) calculations were carried out under criterion for the convergence of the total energy of 5×10^{-4} eV/atom and 0.001 GPa for pressure. The plane-wave kinetic cutoff-energy, E_{cut} , was set to be 480 eV. The first Brillouin zone is sampled into k-grids of 6 x 6 x 6 using the Monkhorst-Pack scheme [32]. Before calculating electronic properties, equilibrium states of the atomic positions at the minimum total energy were obtained using the Broyden-Fletcher-Goldfarb-Shanno optimization algorithm (BFGS) [33-36]. The convergence criteria were set to be 10^{-6} eV/Å, 0.0001 GPa and 0.05 Å, for the Hellmann-Feynman forces, pressure and maximum displacement, respectively. For optical properties, a dense sampling of 18x18x18 of the first Brillouin zone was used where the total number of irreducible k-points is 165.

Hybrid functional of BLYP [37, 38] was implemented in Dmol³ code. We compare the band structure and density of states (DOS) with those by GGA-PBE. Dmol³ is a powerful DFT code that can include dispersion-correction (DFT-D) for van der Waals interaction into BLYP hybrid functional. This has been proven to produce excellent results for silicon clusters in comparison with LDA [31]. The range of global orbital cutoff scheme was set to be 4.6 Å, and dispersion-correction proposed by Tkatchenko and Scheffler [39] was used. A polarization *d*-function is added to each silicon atom through the use of a double numerical plus polarization basis set (DNP) [40]. The calculated lattice parameters were taken from the fully-optimized structure calculated by GGA-PBE in CASTEP code, and then self-consistent calculations were performed by using dense k-sampling meshes of (10 x 10 x 10) with 75 irreducible k-points. The valence electronic configurations of each

Si atom are chosen to be Si:[Ne] $3s^2 3p^2$ [28]. It is important to consider that the effects of polarizations from the d -orbitals are added for silicon atoms within the BLYP functionals [31]. In this case, the electronic configuration of silicon atoms will be set as (Si: $1s^2 2s^2 2p^6 3s^2 3p^2 4s^1 3d^1$), where the $Si-4s$ and $Si-3d$ orbitals are empty and used as ‘virtual orbitals’ in order to enhance the charge redistribution, which gives better estimation for the electronic properties. In this work, we have chosen 60 empty bands for setting the conduction bands in both clathrates to calculate optical properties.

II.2. Structural details

II.2.1. Type-I Si_{46}

The type-I silicon clathrate with a chemical formula of M_8Si_{46} has a cubic structure with the space group of Pm-3n (#223), where the guest-free Si_{46} unit includes 46 atoms, which can be formed by a compact arrangement of eight face-sharing cages: two dodecahedrons Si_{20} (a ‘platonic’ solid with twelve pentagonal faces and 20 atoms, usually referred to as: $[5^{12}]$), plus six tetrakaidecahedron Si_{24} (12 pentagonal faces and two hexagonal faces with 24 atoms symbolized as: $[5^{12}6^2]$) [3, 13, 41]. The vacant cavities inside the cages are usually filled by “guest” atoms such as alkaline or alkali-earth metal species. In this structure, the “host” silicon atoms occupy three Wyckoff positions: 6c, 16i, and 24k, while the guest atoms occupy the 2a and 6d positions of the space group. In this study, no guest atoms are considered. Figure.1a shows a unit cell of type-I X_8Si_{46} including the Wyckoff positions. Figure.1c illustrates the two initial polyhedrons forming the Si_{46} main lattice. To determine the equilibrium lattice constants of type-I Si_{46} theoretically, we carried out lattice optimizations by calculating stress tensors. The optimized lattice parameter within GGA-PBE is $a = 10.23 \text{ \AA}$. As listed in Table.1, our obtained results are compared with those calculated by different first-principles methods. As no experimental data for guest-free type-I and VIII Si_{46} is available at the present, we employed our experimental structures of Ba_8Si_{46} and $Ba_8Cu_4Si_{42}$ for type-I and VIII, respectively, as an initial structure for the lattice optimizations. [12, 42] ($a = 10.33$ and $10.32 \text{ \AA}$, respectively). The volume difference between our optimized Si_{46} and the experimental Ba_8Si_{46} structures is attributed to the size of the barium guests [43].

II.2.2. Type-VIII Si_{46}

Type-VIII silicon clathrate with the same chemical formula as for the type-I phase (allotropic forms of the same clathrate compound), crystallizes in the body-centered cubic with the space group of I4-3m (#217). Main framework of type-VIII clathrate is formed by the combination of only one type of strongly-distorted dodecahedral cages (S_{23}), the host atoms of silicon occupy four Wyckoff

positions: 2a, 12d, 24g and 8c, whereas, the guest atoms M occupy the 8c sites. Figure 1b shows the configuration of a unit cell of type-VIII M_8Si_{46} silicon clathrate. The dodecahedral cages forming the main unit cell of type-VIII Si_{46} are illustrated in the Figure 1d. The equilibrium lattice parameters of type-VIII Si_{46} (VIII- Si_{46}) was obtained within GGA-PBE by using the same BFGS procedure with the same parameter sets as for clathrate type-I. The optimized lattice constant is $a = 10.10 \text{ \AA}$, which is smaller than the type-I, Our values are in a fair agreement with the literature shown in table.1. The optimized bond length range was 2.35-2.42 $\text{\AA}$. Similarly to the I- Si_{46} clathrate, no experimental data is available for neither the guest-free nor for the binary type-VIII X_8Si_{46} silicon clathrate. Since only framework-substituted type-VIII was successfully synthesized, we employed experimental lattice parameters of the ternary silicon clathrate single crystal of $Sr_8Al_xGa_{16-x}Si_{30}$ ($a = 10.44 \text{ \AA}$) reported by Shimizu *et al* [19] .

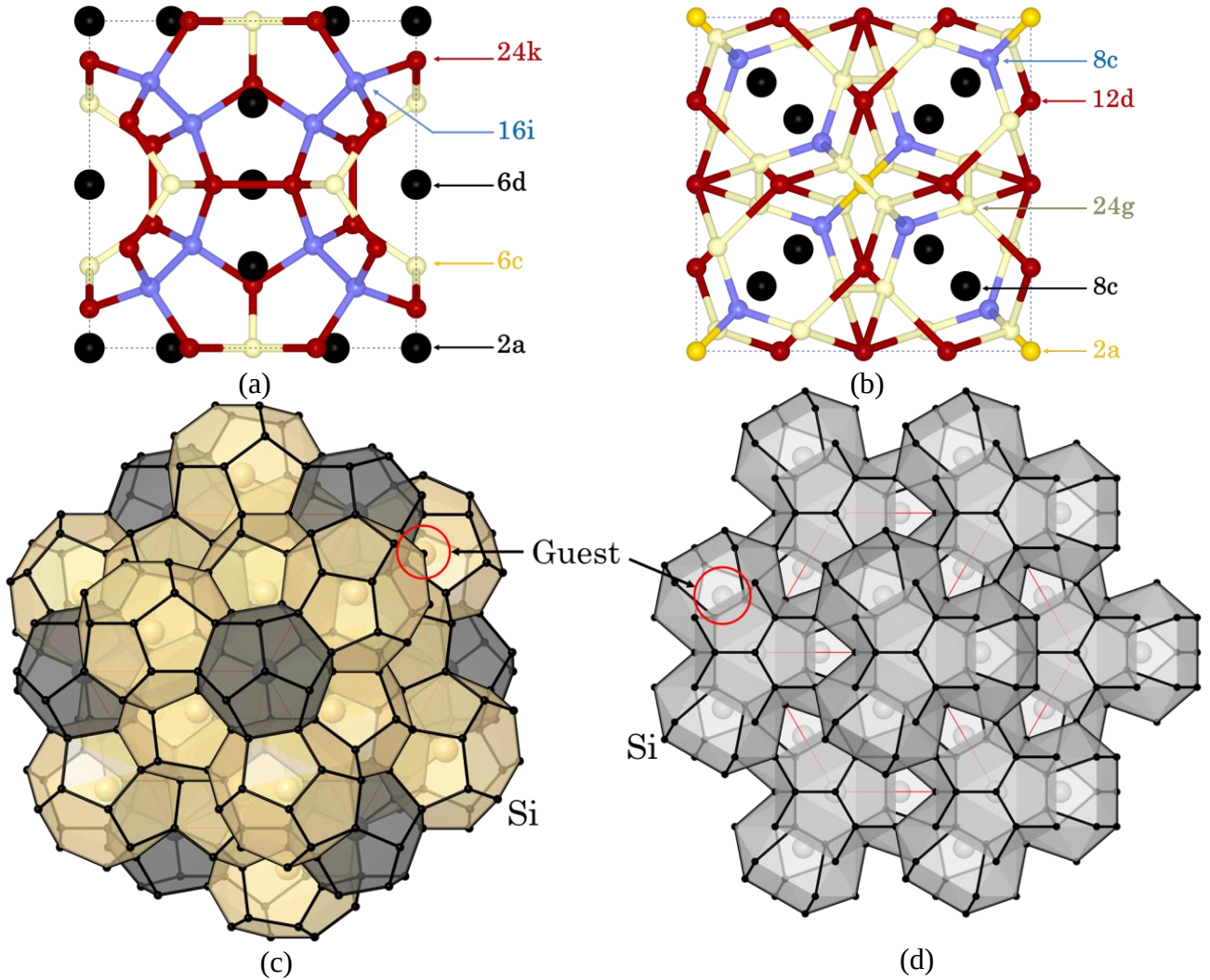


Figure 1. Crystal structures of type-I (a) and type-VIII (b) guest containing silicon clathrates X_8Si_{46} , with Wyckoff atomic positions, (the dark gray balls are guest atoms X). Polyhedral representation of type-I (c) and type-VIII (d) guest-free Si_{46} down the (111) direction.

Table 1. Lattice parameters, bond-length, mass densities, bandgaps, and positions of VBM and CBM for guest-free silicon clathrate Si₄₆ in type-I and -VIII phases as calculated by GGA-PBE and BLYP in comparison with the literature.

	Type-I Si ₄₆	Type-VIII Si ₄₆
Space group	Pm3-n (No223)	I4-3m (No 217)
Lattice parameter $a(\text{\AA})$	10.233 ^a 10.229 ^b 10.355 ^c 10.19 ^d 10.229 ^e 10.317 ^g 10.40 ^j	10.1002 ^a 10.10 ^b 10.1015 ^e 10.10 ^f
Si-Si distance range ($\text{\AA}$)	(2.357 - 2.402) ^a (2.380 - 2.430) ^c	(2.353 - 2.417) ^a
Density $\rho (g.cm^{-3})$	2.01 ^a 2.004 ^b	2.12 ^a 2.082 ^f
Bandgap energy $E_g (eV)$	1.38 ^a (1.620) ^a 1.314 ^b 2.5 ^c 1.26 ^d 0.9 ^h 1.315 ⁱ 1.31 (1.95) ^k	1.36 ^a (1.62) ^a 1.24 ^b 1.24 ^f
Nature of bandgap	Indirect	Indirect
VBM@	Γ -X ^{a,d,h,i}	N (1/2, 0, 0) ^{a,b}
CBM@	Γ -X ^{a,d,h,i}	Γ -H ^{a,b}
a: Our results by GGA-PBE and (GGA-BLYP) b: Data from ref [15] GGA-PBE c: Data from ref [44] Tight binding-like Molecular Dynamics TBMD d: Data from ref [43] LDA e: Data from ref [20] GGA-PBE f: Data from ref [45] GGA-PBE g: Data from ref [46] Molecular Dynamics MD-Lennard-Jones (LJ)Potentials h: Data from ref [47] LDA-LAPW i: Data from ref [48] GGA j: Data from ref [49] Hartree-Fock HF k: Data from ref[50] GGA-PBE and (HSE)		

Table 2. Atomic positions (Wyckoff notation) of type-I and type-VIII guest-free clathrates (Si₄₆) as optimized by GGA-PBE in comparison with the literature.

Si ₄₆ -I		Si ₄₆ -VIII	
6c (x, y, z)	(0.25, 0, 0.5) ^{a,b,c,d}	2a (x= y= z)	(0) ^{a,b,c}
16i (x= y= z)	(0.1836) ^a (0.684) ^b (0.186) ^c (0.1837) ^d	8c (x= y= z)	(0.36455) ^a (0.384) ^b
24k (x, y, z)	(0, 0.308, 0.1170) ^a (0,0.883,0.692) ^b (0, 0.307, 0.1176) ^c (0,0.1172, 0.3077) ^d	12d (x, y, z)	(0.25, 0.5, 0) ^{a,b}
		24g (x=y, z)	(0.415, 0.143) ^{a,b}
a: Our results (GGA-PBE) b: Data from ref [20] GGA-PBE c: Data from ref [49] Hartree-Fock (HF) d: Data from ref [44] Tight binding-like Molecular Dynamics TBMD			

II. Results and discussion

III.1. Electronic properties

Calculated band structures and densities of states (DOS) for type-I and type-VIII Si_{46} using GGA-PBE are plotted in Fig. 2, and band structure with BLYP hybrid functional are shown in Fig. 3. The bandgaps for the type-I and VIII- Si_{46} within GGA-PBE (BLYP) are 1.38 eV (1.62 eV) and 1.36 eV (1.61 eV), respectively. The band gaps calculated with BLYP are generally larger than that with GGA-PBE. Both materials exhibit semiconducting (insulating) behaviors with indirect band gaps in the optimum visible range of the electromagnetic spectrum. Our results are in fairly good agreement with previously reported data (table.1). The conduction band minimum CBM and the valence band maximum VBM of the type-I clathrate are both located at a k -point along the Γ -X line (Figure 2c), in agreement with reference [43]. On the other hands, in the type-VIII Si_{46} , the VBM is located at N-point (1/2, 0, 0) and the CBM appears along the Γ -H line (figure 2d), our result agreed with a previous report [15]. In the valance band (VB) of type-I Si_{46} , the energy bands from Γ to R point are degenerated, and the valence band valleys at X, M, R and Γ are lower in energy than the VBM by 0.06, 0.20, 0.53, and 0.13 eV respectively. For the type-VIII, the VB valleys for the H, P and Γ points are located below the VBM by 0.21, 0.04, and 0.39 eV, respectively.

For type-I Si_{46} , the VB can be subdivided to two major regions separated by a small energy gap estimated at 0.47 eV by GGA-PBE. As shown in Figure 4a, In the partial density of states (PDOS) calculated by GGA-PBE, the lower valence band (LVB: from -11 eV to -4 eV) is composed from large contributions of 3s and small amount from 3p orbitals, whereas the upper valence band (UVB) from -3 eV to 0 eV has large contributions from the 3p-states and very small contribution from the 3s-states of silicon atoms. In contrast, the VB of type-VIII Si_{46} is continuous. As shown in the figure 4b (upper part), the majority of the contributions are from 3p-states, while contributions from 3s-states are noticed to increase when going toward lower energies. The conduction bands for both type-I and type-VIII Si_{46} , are dominated by large contributions from 3p-states and smaller contributions from the 3s-states as depicted in Figure 4. Differences in the electronic properties of the two clathrates are directly related to the nature of their polyhedral cages, the way they combine and the nature of their respective polygonal faces. In type-I Si_{46} , two types of cages combine to form the main lattice (dodecahedron Si_{20} + tetrakaidecahedron Si_{24}). The Si_{20} contains twelve pentagonal rings [5¹²] and the Si_{24} cage contains twelve pentagonal rings plus two hexagonal faces [5¹²6²]. In this case, the dodecahedrons are not related to each other but are connected to other Si_{24} cages through the pentagonal faces only, while the Si_{24} cages are connected to each other by sharing their

two six-fold hexagonal faces. They form a sort of long columns along the three crystallographic directions, as described by Dolyniuk *et al* [13]. The type-VIII lattice is formed by the association of only one type of strongly distorted dodecahedral cages Si_{23} , which, additionally to the five- and six-fold rings, possess three non-flat seven-fold rings (Si_{23} is described as: $[5^3 6^3 7^3]$). In the type-VIII structure, the cages are connected mainly through sharing their pentagonal faces, as each cage has three of them, it will connect with three other cages thoroughly, while it will connect to other cages through non-flat six- and seven-fold faces. This imperfect yet solid inter-cage connection, leads to the formation of inter-cage cavities (vacant 8-vertex polyhedral cages). The main structural differences discussed herein are directly correlated with major differences in the physical and chemical properties.

The main differences in band structures between type-I Si_{46} clathrate and the Si_2 diamond structure, is due to the fact that there are only six-fold polygonal rings in the Si_2 lattice, while in the type-I Si_{46} clathrate lattice, 87% are six-fold and 13% are five-fold rings [43]. Thus, for the Si_2 lattice, the valence band is continuous and larger due to the significant overlap of the 3s- and 3p-states (-12 eV to 0 eV), whereas, for type-I Si_{46} , the presence of the five-fold rings prevent the s-orbitals from forming complete anti-bonding states. The highest 3s-like state is therefore lower in energy than that of the Si_2 , and becomes lower than the lowest 3p-like state leading to an opening of a gap between 3s- and 3p-like states. An extensive analysis of the electronic signature of the pentagonal rings in silicon clathrate was carried out by Mélinon *et al* [51]. By combining experimental and theoretical work, they demonstrate that the introduction of pentagonal rings into the diamond lattice induces a merging of the s- and sp-like bands, which reduce the valence band width. Similar analysis can be inferred from our results. In type-VIII Si_{46} lattice contains only one type of strongly distorted dodecahedron Si_{23} , which is derived by breaking three edges and adding three new vertices to the regular pentagonal dodecahedra Si_{20} [13]. Such a dodecahedral cage is equally composed by one third of five-folds, one third of non-flat six-folds and one third of non-flat seven-fold rings (see Figure5). The presence of seven-fold rings will allow the s-states to overlap again with the 3-p states to make the valence band continuous yet larger than that of the type-I counterpart. Therefore, the bandgap of type-VIII Si_{46} is slightly smaller than the type-I bandgap as also predicted by Norouzzadeh *et al* [15].

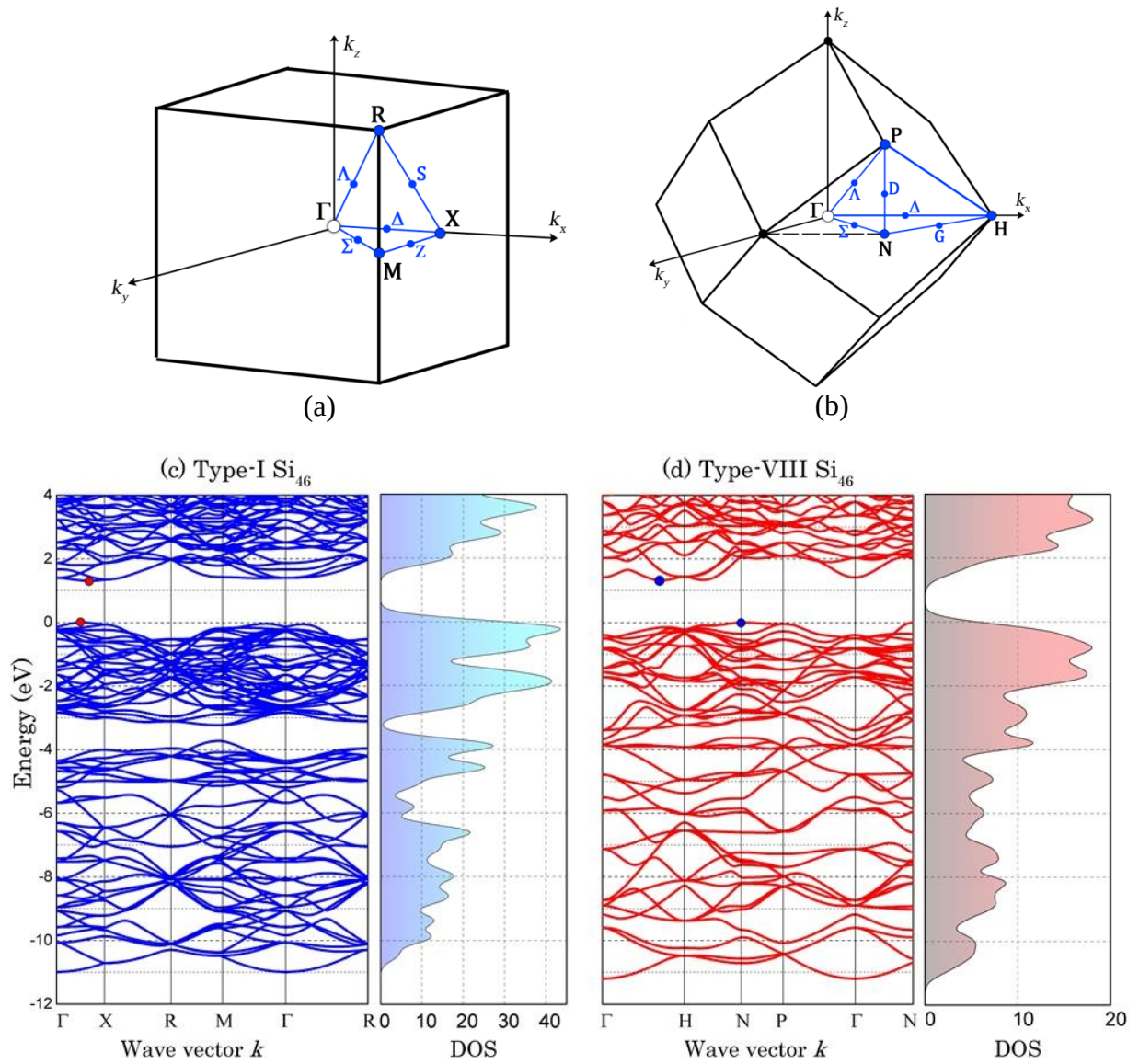


Figure 2. First Brillouin zones of (a) type-I (Pm3-n) and (b) type-VIII (I4-3m) cubic clathrates obtained through their reciprocal lattices. Band structures and total density of states (DOS) of (c) type-I Si_{46} within GGA-PBE, the band structure is calculated along the symmetric line of $\Gamma(0,0,0)$ - $X(1/2,0,0)$ - $R(1/2,1/2,1/2)$ - $M(1/2,1/2,0)$ - Γ - R . (d) Band structure and total density of states (DOS) for type-VIII Si_{46} within GGA-PBE along the symmetric line of $\Gamma(0,0,0)$ - $H(1/2,1/2,-1/2)$ - $N(1/2,0,0)$ - $P(1/4,1/4,1/4)$ - Γ - N .

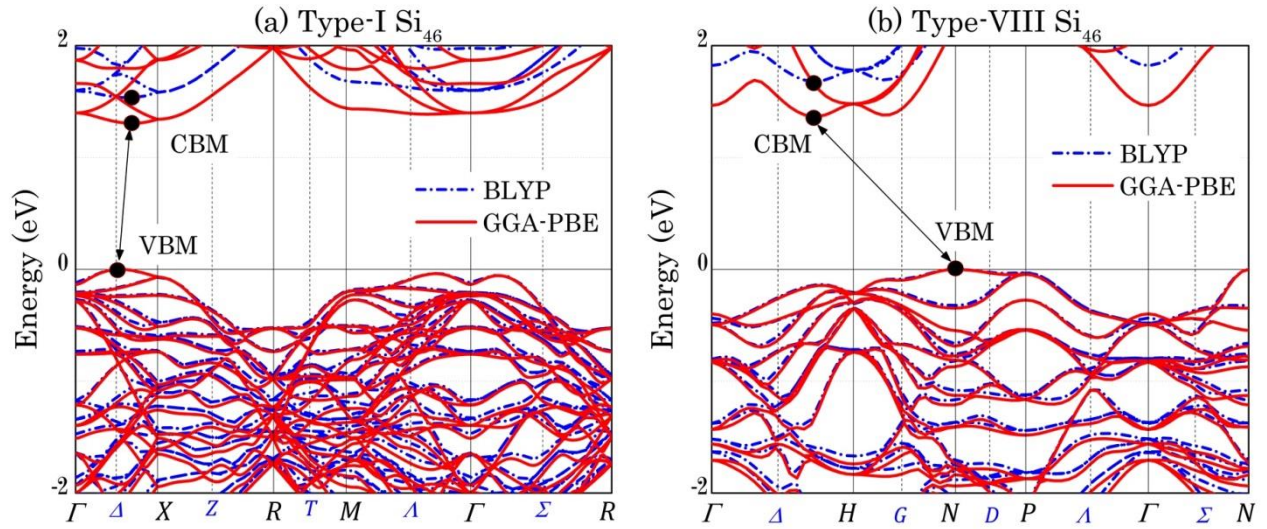


Figure 3. (a) and (b) represent the comparison between GGA-PBE (CASTEP) and BLYP (Dmol³) band structures along the Γ -X-R-M- Γ -R and Γ -H-N-P- Γ -N k -paths for type-I and type-VIII Si_{46} clathrates respectively. The Fermi energy is set to be the zero energy reference.

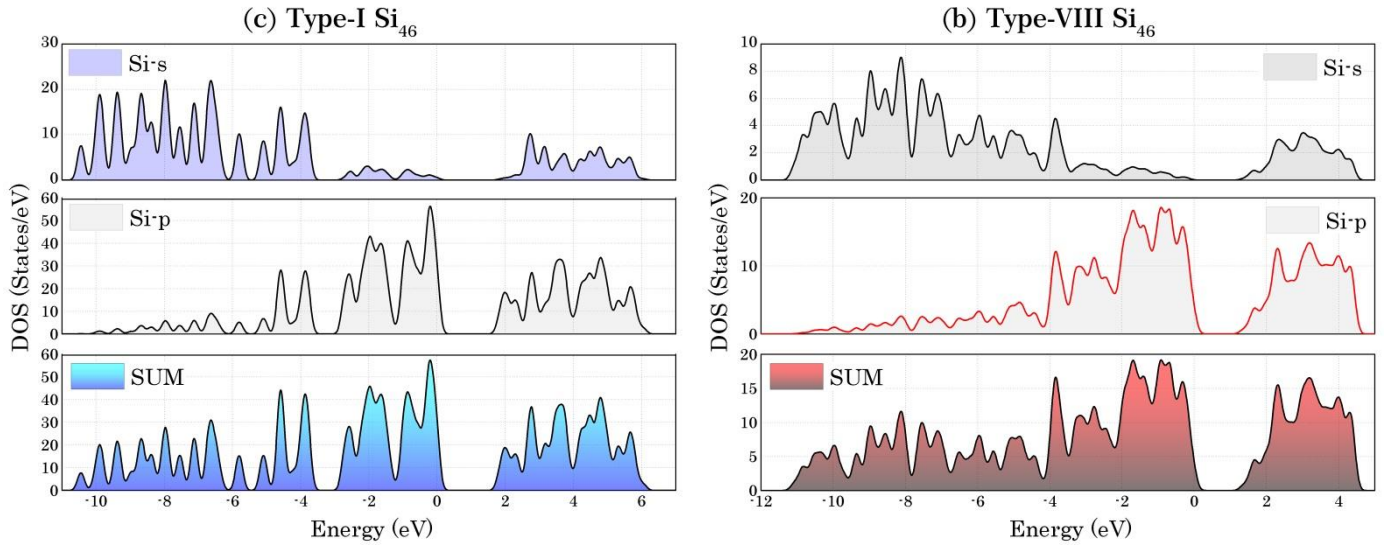


Figure 4. Partial and total densities of states (DOS) for (a) type-I and (b) type-VIII guest-free silicon clathrates Si_{46} calculated by GGA-PBE using CASTEP package.

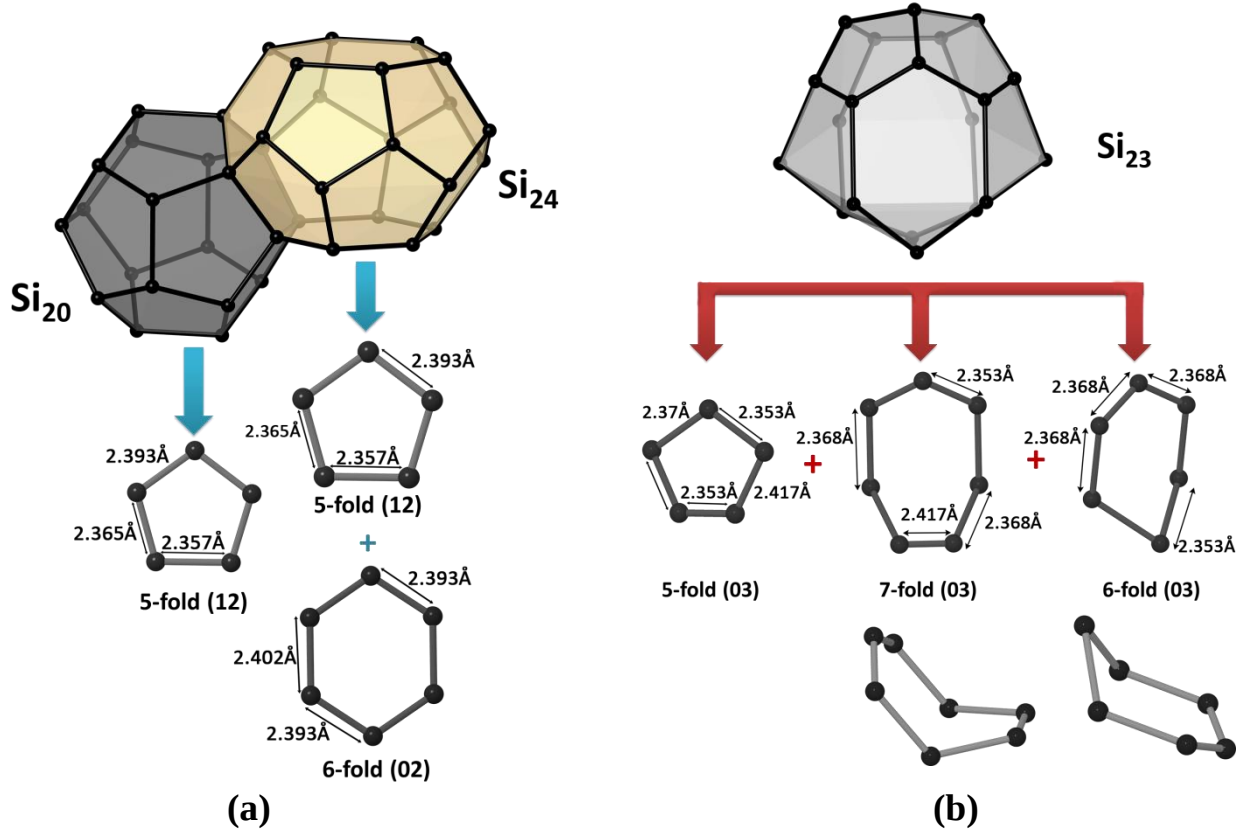


Figure 5. Elemental polyhedral cages and their respective polygonal faces and their numbers (between parentheses) in each cage for: (a) type-I and (b) type-VIII Si_{46} . The seven- and six-fold rings in the type-VIII material are not flat due to the strong distortion of the dodecahedrons Si_{23} .

III.2. Linear optical properties

The indirect nature of the band gaps of both silicon clathrate materials is considered as a limiting factor regarding their use for photonics or photovoltaics. Inducing an indirect-direct bandgap transition in type I clathrate was already predicted through the effect of biaxial tensile strain [52]. This prediction could be experimentally verified if an appropriate substrate was chosen for the growth of silicon clathrates in thin film form, which could open a plethora of applications for an all silicon materials in optoelectronics. However, there are only few studies on the optical properties for type-I so far, and actually still no data are available on the type-VIII Si_{46} clathrate. In the present part of the work we attempt to clarify some fundamental optical properties for both clathrates in their equilibrium states at ambient pressure.

Optical properties of materials are expressed through the frequency-dependent dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. It represents the linear response of the material to an external electromagnetic field. It is strongly related to the photon-electron interaction within the matter [53]. The imaginary part $\varepsilon_2(\omega)$, is computed from the matrix elements that taking all possible transitions between the

occupied and unoccupied wave functions within the Fermi's golden selection rules, which can be written by using the following formula [54, 55],

$$\varepsilon_2(\omega) = \left(\frac{4e^2\pi^2}{m^2\omega^2} \right) \sum_{ij} \int \langle \psi_i | M_{if} | \psi_j \rangle^2 f_i (1 - f_i) \delta(E_f - E_i - \omega) d^3k \quad (1)$$

where ψ_i and ψ_j represent the initial and final states respectively, M_{if} is the dipole operator, f_i is the Fermi distribution function for the i^{th} state and E_i is the energy level of the valence electron in this eigenstate. The real part $\varepsilon_1(\omega)$ is extracted from the imaginary part through the Kramers-Kronig formulation [54, 55]:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega') d\omega'}{(\omega'^2 - \omega^2)} \quad (2)$$

In this study, we have computed the dielectric functions as well as the absorption coefficients for the theoretically optimized structures of both guest-free Si_{46} clathrates. Figure 6 (a) and (b) display the imaginary and real parts of the calculated dielectric function, respectively. In both clathrates, the imaginary part of the dielectric function $\varepsilon_2(\omega)$ is located in the energy range of 0 to 8 eV. The absorption edge of type-VIII is positioned at lower energy than that for the type-I. The difference of threshold energies corresponds to band gap values of 1.377 eV and 1.360 eV, approximately.

The $\varepsilon_2(\omega)$ curves exhibit sharp spectrums where the maximum peaks are located at 3.27 eV (3.34 eV), and the second peaks are located at 3.97 eV (3.59 eV) for type-I (type-VIII) Si_{46} . In order to determine the origins of the peaks, here we consider only the direct interband transitions and neglect the indirect phonon-assisted transitions. For both clathrates, due to the strong sp^3 bonding of the silicon networks, the main peaks of $\varepsilon_2(\omega)$ are all generated from the electronic transitions from the top of the valence band to the bottom of the conduction bands along the corresponding valleys in the high-symmetry k-vector path. For the type-I Si_{46} , the first peak originates from the Si-2p (-0.5 eV) to Si-3s (1.87 eV) interband transitions at the R point, however, It has been reported that the optical interband transitions in the type-I Si_{46} are shown to be dipole-forbidden along Γ , Γ -X(Δ) and X-M(Z) high symmetry points [56]. Whereas located at 2.46 eV for the type-VIII Si_{46} , the first small peak may originate from the Si-3p (-0.45 eV) to Si-p (1.85 eV) transition at the Λ low-symmetry point. The real part of the dielectric function $\varepsilon_1(\omega)$ is plotted in the Fig. 6 (b) and shows similar behavior for both materials with slightly higher values for the type-VIII Si_{46} . Major peaks appear at 2.71 eV and 3.06 eV and the minimum peaks are at 4.97 eV and 5.23 eV for type-I and type-VIII respectively. The zero frequency limit of the real part $\varepsilon_1(0)$, which represents the electronic part of the static dielectric constant that strongly depends on the bandgap magnitude and nature, is

estimated in our case as 11.24 and 12.3 for type-I and type-VIII Si₄₆ respectively. Additionally, $\epsilon_1(\omega)$ becomes negative within the ranges of 4.07 to 13 eV (4.20 to 13 eV) for type-I (type-VIII) Si₄₆, and both figures tend toward zero for higher energies.

Several recent studies has proven that group-IV clathrates can provide high absorption coefficients[9, 57-59] compared to their diamond phase counterpart. Silicon clathrates can be promising candidates used for optical, optoelectronic and photovoltaic applications. Figure 7 illustrates the optical absorption as a function of the incident light energy for type-I and -VIII Si₄₆ in the range of 0-18 eV. The fundamental absorption edges are located at 1.24 eV and 1.20 eV, whereas, the maximum peaks are positioned at 5.26 and 5.27 eV for type-I and type-VIII Si₄₆ respectively. After reaching their maximum values, absorption coefficients for both materials start decreasing rapidly toward zero, which is a characteristic for semiconducting behavior. We have computed the absorption coefficients for type-I and type-VIII Si₄₆ by means of GGA-PBE using 18 x 18 x 18 dense sampling of the first Brillouin zone giving 165 k-points for each system. The absorption coefficient represents a measure of the rate of decay in the light intensity that crosses the material. It is usually expressed as a fraction of absorbed light energy per distance unit (cm⁻¹). It is directly derived from the complex dielectric function through the formula (12) given by

$$\alpha(\omega) = \frac{2k\omega}{c\hbar} \quad (3)$$

where: ω and c are the incident light frequency and the speed of the light in vacuum respectively.

For type-VIII the absorption spectrum is slightly lower in magnitude than its type-I. Our calculations of the absorption coefficient and the dielectric function demonstrate a great potential for optical applications for both type-I and type-VIII structures. This may invite further experimental and theoretical research for possible applications in photovoltaic or photonic devices.

III.3. Symmetry analysis and optical transitions

In this section, we study the dipole-allowed optical transitions by means of symmetry-analysis by using GGA-PBE results. Firstly, we have to consider our materials as pure periodic crystals as the symmetry-analysis is held within the bulk form. Symmetry-analysis study is primordial in order to have a deep insight of the possible direct optical transitions that can be (if dipole-allowed by symmetry) a factor in favor of using the investigated materials for photovoltaic and photonic devices. Furthermore, symmetry-analysis allows us to evaluate the interband transitions and the symmetry of the important energy bands and their respective point groups at high and low symmetry points in the Brillouin zone. Conn  table[56] has extensively investigated, the optical transitions for

intercalated and empty type-I X_8Si_{46} and type-II X_6Si_{34} silicon clathrates ($X=Xe, I, Te, Sn$) using symmetry-analysis from LDA results [56]. It has been demonstrated that most of the interband transitions are dipole-forbidden at the band edges in type-I and type-II clathrates except for the type-II Xenon-doped Xe_6Si_{34} clathrate at the low symmetry point $\Lambda(C_{3v})$, where the transition was found to be dipole-allowed. However, analysis of the optical transitions for the type-VIII Si_{46} has not been reported so far. In the following, we present a study of the interband optical transitions in both clathrates type using the group theory approach. As discussed previously, the VBM and CBM for type-I are both located within the Γ -X line, whereas, they are respectively located at N and Γ -H line for the type-VIII Si_{46} . The symmetries of the first three valence bands and the two first conduction bands, at several high- and low-symmetry points in the first Brillouin zone are taken in consideration for both clathrates. The wave-vector path along the high symmetry points of (Γ, X, M, R, H, N, P) were chosen by using the compatibility relations tables available in the literature for the simple cubic SC (type-I, $Pm\bar{3}n$, n°223) and the body centered cubic BCC (type-VIII, $I4_3m$, n°217) systems [60, 61]. We adopt the Schoenflies notations to designate the point groups and their irreducible representations (IRs)[62]. The high and the low symmetry points in the first Brillouin zone of both materials are illustrated in Figure 2.

In type-I Si_{46} , the Γ belongs to the O_h point group, whereas, Δ and Z k-points belong to the C_{4v} and C_{2v} point groups respectively. For type-VIII Si_{46} , the Γ belongs to the T_d point group, while the points H, N, and P have the T_d , the C_{2v} and the T_d symmetries respectively. The point groups of the low symmetry points for VIII- Si_{46} i.e. the Δ , G, D, Λ , Σ are the C_{2v} , C_s , C_{2v} , C_{3v} , and C_s symmetries, respectively. The irreducible representations (IRs) for each point group are taken from character of wavefunctions at each k-point. For the VIII- Si_{46} at the $\Gamma(T_d)$, the first valence band has the A_2 representation, the second and third valence bands are merged together at Γ and they have the T_2 representation. The upper valence bands are mainly constructed from 3p orbitals and minor contributions from 3s-states. At this region, the Γ , H and P k-points of the upper valence bands tend to merge (see figure 8). In contrary, at low symmetry k-points energy bands tend to separate except for Δ and Λ lines. This is due to the hybridization mechanism with anti-symmetric combinations of the s and p-orbitals, which is similar to the hybridization mechanism in the type-I Si_{46} and in other Si clusters as well [56]. The IRs at Γ for the first conduction band in type-VIII Si_{46} is A_1 and the second conduction band has the T_2 symmetry. Table 3 lists the symmetry classifications of the point groups, the energies and the IRs for each energy band near the Fermi level for both types of clathrates.

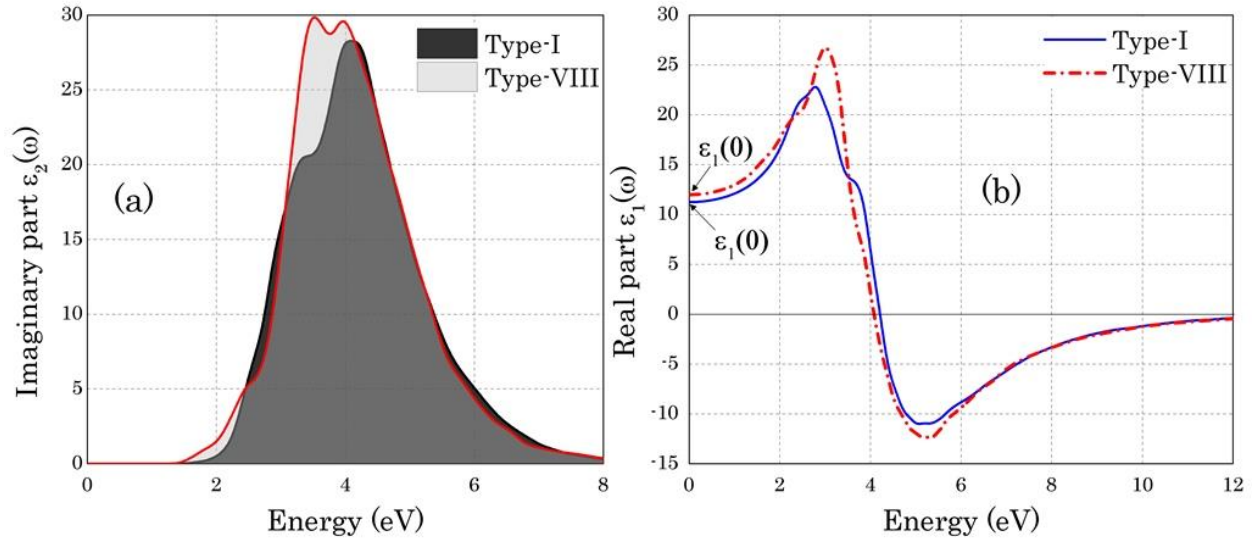


Figure 6. (a) Imaginary and (b) real parts of the complex dielectric function calculated by GGA-PBE as a function of the energy for type-I and type-VIII Si_{46} clathrates.

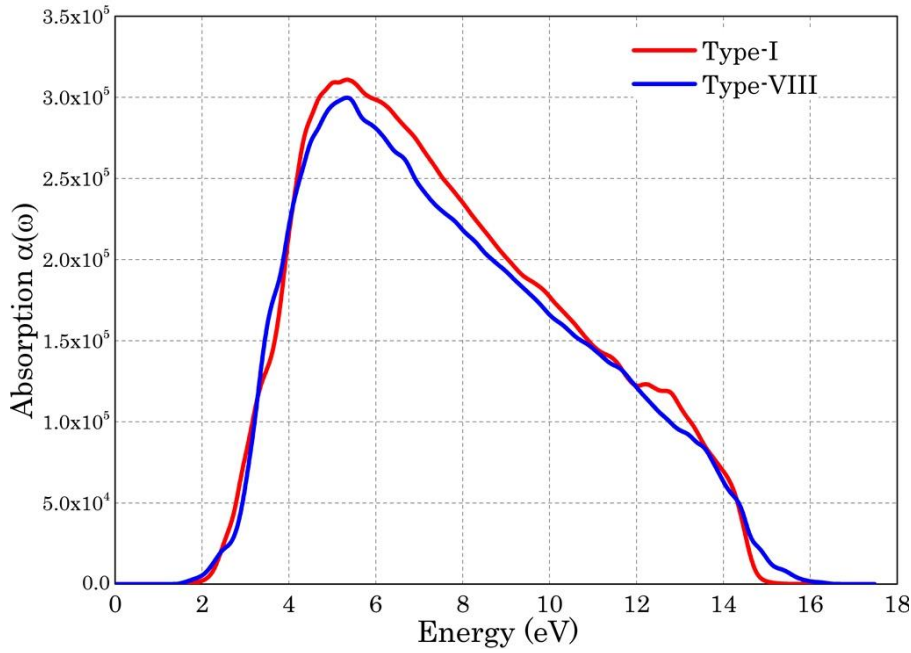


Figure 7. Optical absorption as a function of energy calculated by GGA-PBE for type-I and type-VIII Si_{46} clathrates.

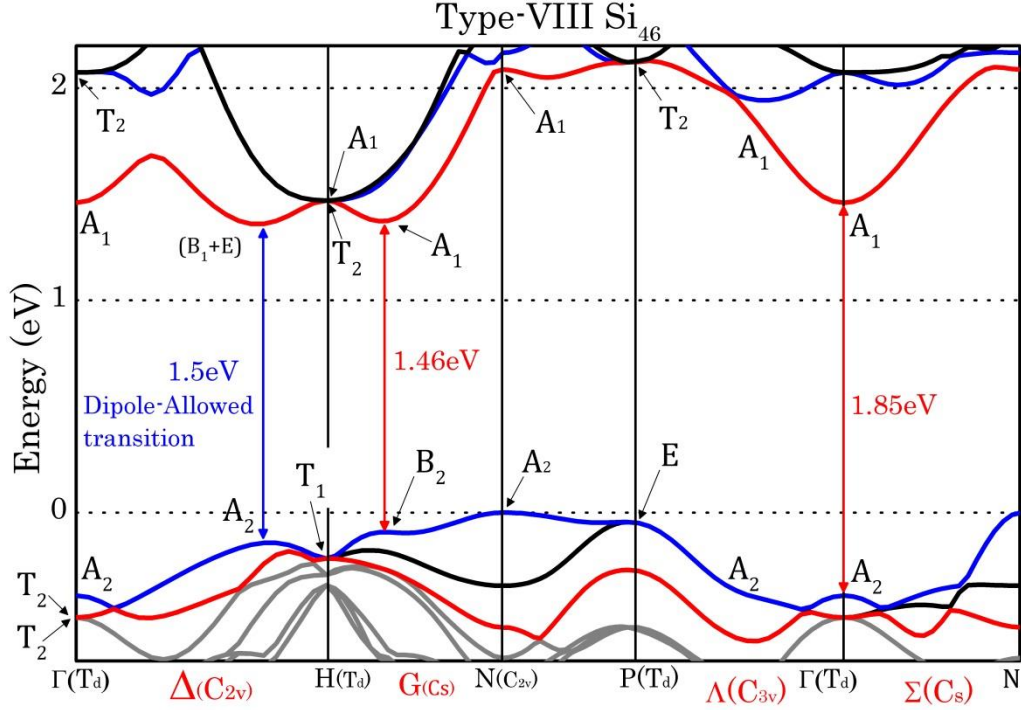


Figure 8. Symmetry classifications of energy bands for the type-VIII Si_{46} clathrate.

In order to investigate the dipole-allowed or forbidden interband transitions, we apply the selection rules for both type-I and type-VIII allotropes. The probability magnitude of the electric dipole transition per unit of time between an initial $|\psi_i\rangle$ and a final $|\psi_f\rangle$ state is proportional to the dipole matrix elements [63]:

$$M_{if} = \langle \psi_i | P | \psi_f \rangle \quad (4)$$

Where: P is the electron momentum operator. Calculating the direct-product of the two irreducible representations involved in the dipole matrix elements using the character tables together with the selection rules, will permit us to determine those interband transitions which are either allowed ($M_{if} \neq 0$) or forbidden ($M_{if} = 0$). For the type-I Si_{46} , group theory analysis at the $\Gamma(O_h)$, $\Delta(\Gamma-X)$ and $Z(X-M)$, shows that all the interband transitions are dipole-forbidden by symmetry, which is coherent with the results of Connétable [56].

For the type-VIII Si_{46} , the direct products between the irreducible representations of the first valence and conduction bands along the $\Gamma(\text{T}_d)$, $\Delta(\text{C}_{2v})$, $\text{H}(\text{T}_d)$ and $\text{G}(\text{C}_s)$ k-points are calculated and summarized in the table 3. We also include in table 3, the irreducible representations of the momentum operator $P(\text{T}_d)$, which are necessary for the calculations of the dipole matrix elements of the interband transitions. The three components of the momentum operator p_x , p_y and p_z along the Γ - $\text{H}(\text{C}_{2v})$ line belong to the irreducible representation T_2 [64]. As inferred from table 4 and table 5, the

direct product of the irreducible representations at the $\Gamma(T_d)$ point shows that the electronic transition between the first valence band $E_{v1}(A_2)$ and the first conduction band $E_{c1}(A_1)$ through the momentum operator $P(T_2)$ is equal to (T_1) . The direct product at the Γ -H(Δ) line (C_{2v}) between the top valence band $E_{v1}(B_2)$, the momentum operator $P(A_1)$ and the first conduction band $E_{c1}(A_1)$ is equal to (B_2) . According to the selection rules, transitions (from an initial state $|\psi_i\rangle (E_{v1})$ to a final state $|\psi_f\rangle (E_{c1})$) are dipole-allowed if the direct product of the IRs of the VB, the momentum operator P and the CB contain at least one character from the final state's IR [64]. Therefore, interband transitions at Γ point are dipole-forbidden, while they are dipole-allowed by symmetry along the Γ -H (Δ) line. This is a very interesting preliminary result and holds promises for type-VIII Si_{46} clathrate as an optoelectronic material. In particular, with its large number of carrier pockets near the band edges [15], and the possibility to induce an indirect to direct bandgap transition through biaxial strain in thin film form [52], we predict very interesting optical and thermoelectric features for Type-VIII silicon clathrates.

Table 4. Characters of the irreducible representations of the T_d point group. The bottom part represents the direct product between the IRs of the first conduction and valence bands along the $\Gamma(0,0,0)$ k-point for the type-VIII Si_{46} .

IRs		E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear, rotations	Quadratic functions
Γ_1	A_1	+1	+1	+1	+1	+1		$x^2+y^2+z^2$
Γ_2	A_2	+1	+1	+1	-1	-1		
Γ_{12}	E	+2	-1	+2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
Γ_{25}	T_1	+3	0	-1	+1	-1	(R_x, R_y, R_z)	
Γ_{15}	T_2	+3	0	-1	-1	+1	(x, y, z)	(xy, xz, yz)
Direct Product								
$\Gamma_2 \otimes P(T_2) \otimes \Gamma_1$		+3	0	-1	+1	-1	$A_2 \otimes T_2 \otimes A_1 = A_2$ (Forbidden)	

Table 3. Symmetries, point groups and irreducible representations for type-I (O_h) and type-VIII (T_d) Si_{46} silicon clathrates. The energies are calculated from the VBM along each symmetry k -point from GGA-PBE band structures. Between brackets are indicated the Irreducible Representation for each energy band. Point groups symbols are given in Schoenflies notation [62].

Si ₄₆ -I				Si ₄₆ -VIII				
	Γ (O_h)	Δ (C_{4v})	Z (C_{2v})	Γ (T_d)	Δ (C_{2v})	H (T_d)	G(Cs)	N(C_{2v})
Conduction Bands								
	E (eV)			E (eV)				
E_{c2}	+2.00 ^a +1.59 ^b [A _{2g}]	+1.66 ^a +1.45 ^b [B ₁]	+1.92 ^a +1.45 ^b [B ₁]	+2.07 ^a [T ₂]	+2.15 ^a [B ₁]	+1.477 ^a [A ₁]	+1.97 ^a [A ₁]	+2.43 ^a [B ₁]
E_{c1}	+1.63 ^a +1.32 ^b [T _{1u}]	+1.55 [A ₁ +E] ^a +1.23[A ₁] ^b	+1.65 ^a [A ₁ +B ₁ +B ₂] ^a 1.30 ^b [A ₁]	+1.46 ^a [A ₁]	+1.55 ^a [A ₁]	+1.477 ^a [T ₂]	+1.72 ^a [A'']	+2.43 ^a [A ₁]
Valence Bands								
E_{v1}	-0.11 ^a -0.13 ^b [A _{1u}]	0.00 [A ₂] ^a 0.00 [A ₂] ^b	-0.14 ^a -0.15 ^b [A ₂]	-0.39 ^a [B ₂]	-0.153 ^a [B ₂]	-0.2164 ^a [T ₁]	-0.095 ^a [A']	0.00 ^a [A ₂]
E_{v2}	-0.11 ^a -0.23 ^b [T _{2g}]	-0.13 [B ₂ +E] ^a -0.19 [B ₂] ^b	-0.18 ^a -0.20 ^b [A ₂]	-0.49 ^a [T ₂]	-0.30 ^a [B ₁]	-0.2164 ^a [E]	-0.23 ^a [A']	-0.347 ^a [A ₁]
E_{v3}	-0.20 ^a -0.24 ^b [E _u]	-0.22 [A ₂ +B ₂] ^a -0.26 [E] ^b	-0.23 [A ₂ +B ₁] ^a -0.33 [B ₂] ^b	-0.49 ^a [T ₁]	-0.31 ^a [A ₁]	-0.2164 ^a [T ₂]	-0.331 ^a [A']	-0.541 ^a [B ₁]
Irreducible representation of the electron momentum operator $P(T_d)$								
	[T _{1u}] ^{a,b}	[E+A ₁] ^{a,b}	[A ₁ +B ₁ +B ₂] ^{a,b}	[T ₂] ^a	[A ₁] ^a	[T _{1g}] ^a	[A''] ^a	[A ₂] ^a
Optical transition?								
	No	No	No	No	YES	No	No	No
<i>a</i> : Our data (GGA-PBE)								
<i>b</i> : data from reference [56](LDA)								

Table 5. Characters of the irreducible representations of the C_{2v} point group. The bottom part represents the direct product between the IRs of the first conduction and valence bands along the Γ -H(Δ) k -point for the type-VIII Si_{46} .

IRs		E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	linear, rotations	Quadratic functions	Cubic functions
Δ_1	A ₁	+1	+1	+1	+1	z	x^2+y^2, z^2	$z^3, z(x^2+y^2)$
Δ_2	A ₂	+1	+1	-1	-1	R_z	-	-
Δ'_1	B ₁	+1	-1	+1	-1	-	x^2-y^2	$z(x^2-y^2)$
Δ'_2	B ₂	+1	-1	-1	+1	-	xy	xyz
Direct Product								
$\Delta_2 \otimes P(A_2) \otimes \Delta_1$		+1	-1	-1	+1	$B_2 \otimes A_1 \otimes A_1 = B_2$ (Dipole-Allowed)		

VI. Conclusions

In this study, we have performed first-principles DFT calculations in order to investigate the structural, electronic, and optical properties of the type-I and type-VIII guest-free silicon clathrates Si_{46} , systematically. We apply hybrid functional approach with Becke, Lee-Yang-Parr (BLYP) functional and compare the electronic properties with those by generalized gradient approximation (GGA-PBE). The band structures of both Si_{46} clathrates show semiconducting (insulating) properties. The band gaps for both the type-I and type-VIII calculated with BLYP hybrid functional are larger than that by GGA-PBE. The main peak of optical absorption in type-I clathrate is slightly larger than that of type-VIII. However, symmetry analysis has demonstrated that the type-VIII Si_{46} has an optically active electronic transition along the Γ -H line that can be a motive for further investigation and strain engineering to obtain great optical material that can be invested for better photonics and thin film silicon solar cells with higher light absorptions and efficiencies.

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APPENDIX A: Experimental work

Synthesis of silicon clathrates: experimental procedures and results

Abstract

This part is dedicated to the representation and discussion of the experimental work that has been done as the second part of the thesis, thus, this includes the synthesis of silicon clathrates in bulk and thin film forms. Experimental methods including arc-melting, thermal decomposition of precursors, thin film deposition are explained. Characterization includes XRD, physical properties measurements PPM (thermoelectric and stress measurements), and microscopy (SEM) are detailed. Final XRD shows a successful synthesis of ternary silicon clathrate through XRD, and thin films are mostly formed from silicides and traces of silicon clathrates. Experimental work was done in Japan (NIMS, Tsukuba), and in Sweden (Albanova, Stockholm university).

1. Introduction

Group-IV clathrates are inclusion compounds where a host framework of group-IV element forms a cage-like structure that holds guest atoms within, mostly a rare-earth, alkaline-earth or alkali-metal species. Bulk, powder or single crystals of type-I and type-II clathrates have been synthesized through diversity of techniques, thin films are however considered as new route. To the best of our knowledge, only fewer works on thin films of clathrates have been reported. We mention hereby the $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ as the first ternary clathrate to be grown as thin film in the type-I configuration by means of laser ablation technique using a crystalline $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ clathrate as target [1, 2]. The film was found to be polycrystalline. Shortly after, $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ was grown by radio frequency RF helicon magnetron sputtering, using also a crystalline $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ target [3] the grown film was also polycrystalline. First thin films of type-I $\text{Na}_8\text{Si}_{46}$ and type-II $\text{Na}_x\text{Si}_{136}$ silicon clathrates were prepared by reaction of Na with Si substrate to form a Na_4Si_4 layer and then with subsequent thermal decomposition clathrate phase was obtained, here two types of Si substrates were used to selectively get the desired type, i.e. Si(100) substrate induces type-I whereas a Si(111) will give a type-II clathrate [4]. Similar technique consisting of preparing Zintl-phase NaSi precursor as a film formed on Si substrate by surface reactions with Na vapor followed by annealing under vacuum to transform the NaSi films into Si clathrates in type-I or type-II was reported [5]. More recently, the first successful growth of a guest-free type-II silicon clathrate is reported, a

Si(111) substrate was used to form a NaSi precursor, then a $\text{Na}_x\text{Si}_{136}$ clathrate film was formed through thermal decomposition, and finally, Na atoms are removed by a heat treatment with iodine [6]. For synthesis of bulk clathrates such as $\text{Ba}_8\text{Si}_{46}$ high pressure and high temperature conditions HPHT are highly demanded (pressure from 3 to 5GPa and temperature up to 800°C) [7]. High pressure can be locally induced using substrate-bending technique by intervention of a metallic layer (Nickel for example) to induce a residual pressure either in compressive or tensile directions regarding the direction of the surface concave[8]. That stress can generate pressures up to 6GPa which would be sufficient to obtain the clathrate phase. Therefore, that residual stress route could be advantageous to grow thin films of clathrates in a simple programmable furnace. As novelty is a key for motivation, we want to undertake the both opportunities to establish at once a clathrate thin film using residual-stress technique which is not yet used. For that purpose, a work-plan is suggested in what follows.

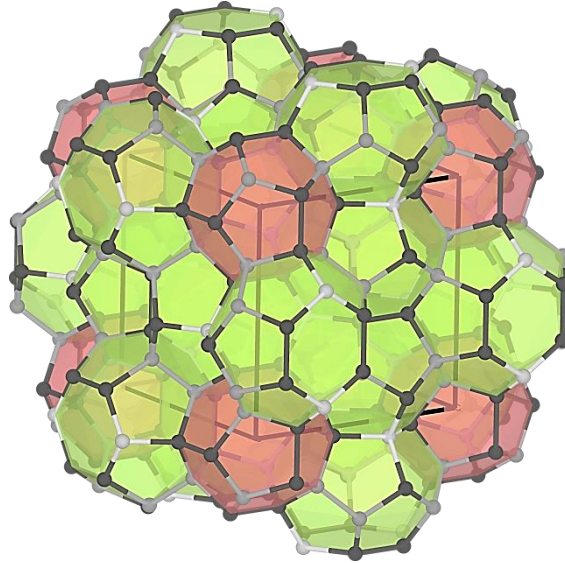


Figure.1. Schematic representation of the (111) and (100) faces of Silicon substrates ($a=5.54\text{\AA}$)

2. Synthesis methods

2.1. Choosing the substrate

In all previous works on clathrates thin films, the substrate was silicon; it is simultaneously advantageous as a support for the film and a source for silicon. According to its orientation (100) or (111), type-I or –II can be obtained. Here we suggest trying them both in order to get the two types.

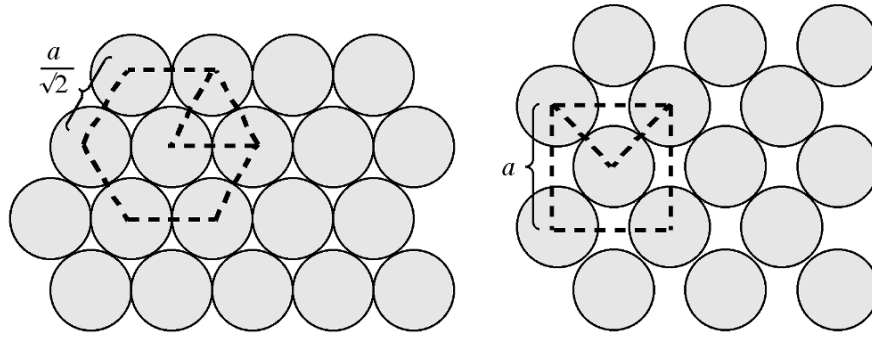


Figure.2. Schematic representation of the (111) and (100) faces of Silicon substrates ($a=5.54\text{\AA}$)

We can go further after having successful results by trying other substrates with larger lattice parameters to induce tensile strain that can provide direct band gap for silicon.

2.2. Guest atoms

Our main objective is obtaining a type-I guest-free silicon clathrate Si_{46} , Barium will be chosen instead of Sodium to conduct the formation of the clathrate configuration, and then will be removed by heat treatment. Ba rods with high purity are very suitable for this task. Noting that Ba atoms are larger than Na (222pm versus 180pm), thus, interaction between Ba and Si framework is stronger than that between Na and Si in clathrates, this will make difficult the removing of Ba from $\text{Ba}_8\text{Si}_{46}$ (but not impossible), therefore, many experiments and tests must be done.

3. The following routes are similar to literature

1. If we chose the thermal decomposition, we will have to expose Si substrate to a Ba vapor, once deposited; we proceed a thermal annealing to form a BaSi_2 film.
2. If we use sputtering technique then we will need BaSi_2 as targets, we can prepare bulk BaSi or BaSi_2 by arc-melting. After preparing precursor or targets, clathrate phase is obtained by thermal decomposition, and Ba atoms can be removed by further heat treatment step, this would be the same method as reported in papers cited in the introduction.
3. Third route is to deposit a thin layer of BaSi_2 on a layer of Aluminum, the system will be annealed under high temperature, clathrate phase could be obtained as Al will facilitate its formation see Fig.2.

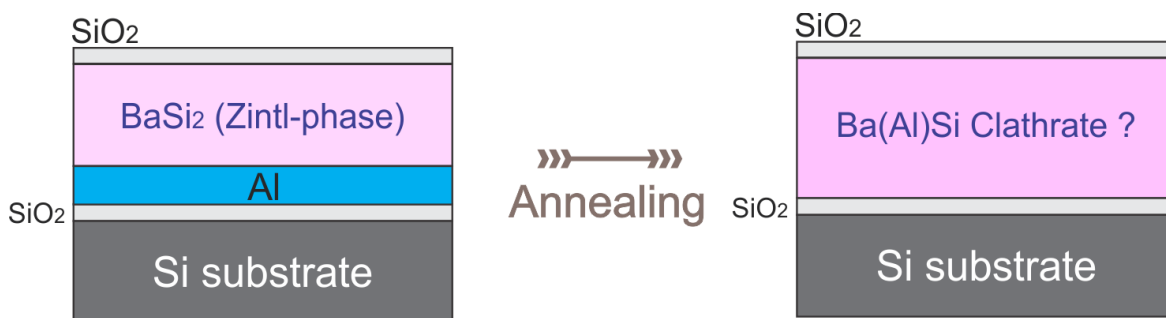


Figure.3. Thin-film formation of clathrate by annealing of BaSi₂ and Al layers.

4. Novel synthesis routes

A ‘novel’ synthesis route was suggested:

- I- Using residual-stress to form the clathrate phase: Ba/Si clathrate are usually synthesized by high pressure high temperature technique HPHT where a pressure between 3 to 5GPa is needed to let the formation of clathrate, thus, by using a residual stress inducer (like Nickel layer) we can exert this pressure without need for special furnace and press, therefore, facilities at NIMS are able to deliver pre-grown Ni films on Si substrate, which will be then coated by protective SiO₂ layer, and then a thin film of BaSi₂ (Zintl-phase Barium di-silicide) will be deposited on top of SiO₂ (Fig.3). Required pressure is applied by appropriate temperature and bending of substrate, thus, a range of **3 to 6GPa** can easily be reached which will be suitable for clathrate phase to form. The SiO₂ oxide layer has a purpose to protect the clathrate layer and prevent the diffusion of Ni atoms into that layer. We have to point that we may add some aluminum beside barium to facilitate the formation of ternary clathrate phase.

4.1. Preparation of Nickel Silicides

100 nm and 150 nm-thick Ni films were separately deposited on two 380μm thick silicon (100) wafers by means of electron beam deposition EBD device at the Mana Foundry. A 50 nm SiO₂ capping layer is finally deposited over the Ni layer by means of sputtering under Argon gas. In order to generate residual biaxial stress that is needed to grow clathrate phases, nickel layers were grown over silicon substrates

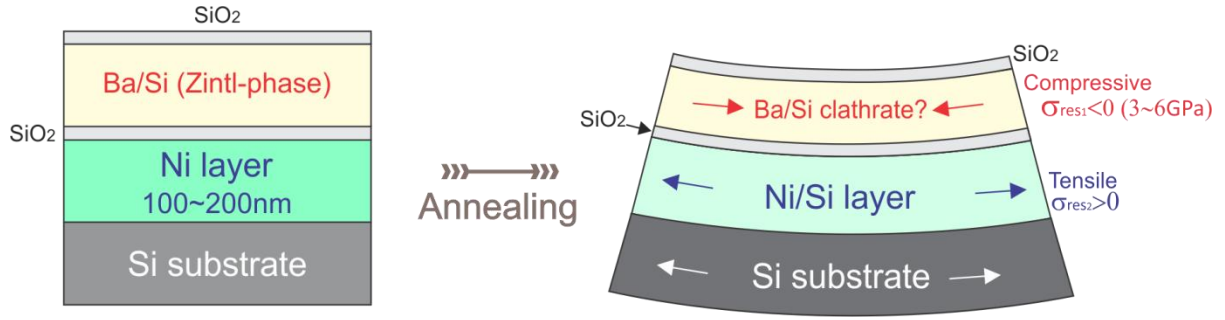


Figure.4. Thin-film formation of clathrate by annealing of BaSi₂ layers.

4.2. Rapid thermal annealing

After deposition of Nickel layers, the substrates are cut into equal square pieces of 13mm x 13mm, Rapid Thermal annealing (RTA) are performed at different temperatures and annealing times using (ULVAC MILA-3000 as shown in figure). Each sample is treated differently, we change the annealing time and temperature and the cooling time as well, for all sample short cooling time is considered in order to generate high residual stress.

4.3. Evaluation of the residual stress

The general stress measurement technique is to use surface profilometry and the Stoney's equation. It consists of measuring the curvature of the substrate before and after a thin film is deposited along the same trace and then to apply the famous Stoney's equation given as:

$$\sigma = \frac{1}{6} \left(\frac{1}{R_{post}} - \frac{1}{R_{pre}} \right) \frac{E}{(1-\nu)} \frac{t_s^2}{t_f}$$

Where

- σ is the residual stress after deposition (GPa)
- R_{pre} is the radius of the substrate curvature before deposition (m)
- R_{post} is the radius of the substrate curvature after deposition (m)
- E and ν are the Young's modulus (130GPa) and the Poisson's ratio (0.28) of the substrate respectively. The term $E/(1-\nu)$ is called the biaxial modulus of the substrate and is equal to 180.5GPa for the Si(100) substrate used in our case.
- t_s is the thickness of the substrate (380 μ m).
- t_f is the thickness of the thin film (100 nm or 150 nm).

In order to evaluate the radius of the substrate's curvature, two dimension surface profiler device DEKTAK (at Mana Foundry) is used to trace the topology of the surface and getting the height of the substrate expressed as a function of the distance along the substrate $y=f(x)$, from this function, the radius of curvature at any point may be calculated as:

$$R = \frac{(1 + y'^2)^{3/2}}{y''}$$

Where $y' = dy/dx$ and $y'' = d^2y/dx^2$

Assuming an initially flat substrate ($R_{pre} \rightarrow \infty$), the residual stress can then be expressed as:

$$\sigma = \frac{1}{6} \left(\frac{1}{R_{post}} \right) \frac{E}{(1-\nu)} \frac{t_s^2}{t_f}$$

Each scan is fit with a 5th order polynomial by the method of least squares. The fit to each scan is then differentiated to produce the function's first and second derivatives. The radius of curvature can then be substituted into Stoney's equation to give a figure of stress.

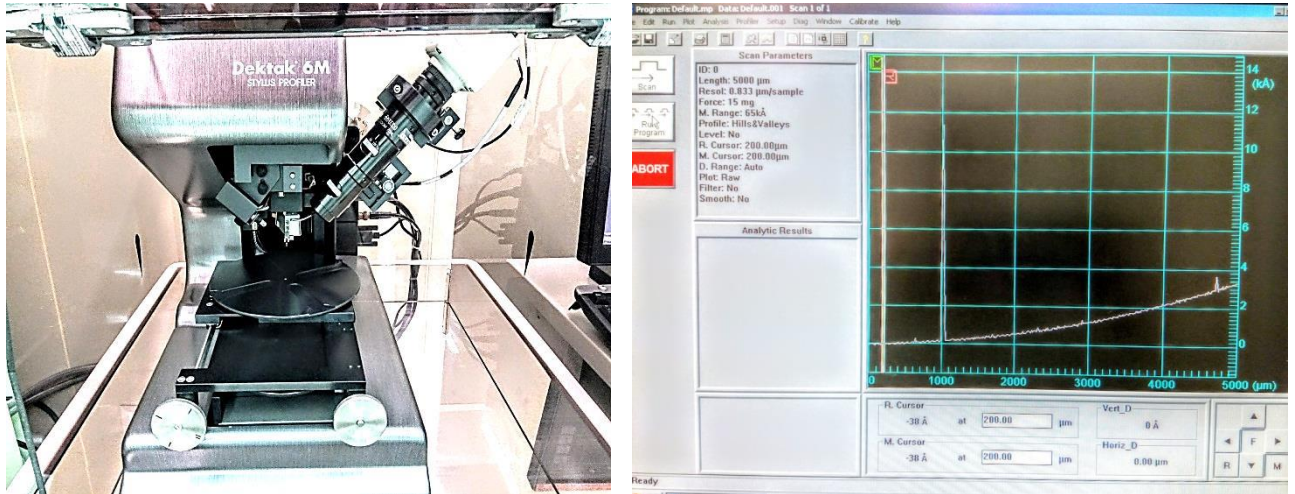


Figure.5. Thin-film formation of clathrate by annealing of BaSi₂ and Al layers.

4.4. Estimation of stress

Our estimations of the residual stress were obtained using the Stoney's equation indicated above. Treatment conditions were from 300°C to 1000°C for different intervals of time. Samples with different RTA conditions are obtained and the calculations of residual stress are all in the range between 0.013GPa to 0.3GPa.

5. Deposition of barium Silicides

After preparing the Ni/Si substrate with two thicknesses of Ni (100nm and 150 nm), barium and silicon are simultaneously deposited by Molecular Beam Epitaxy (MBE). For that purpose, we collaborate with Pr. Takashi SUEMASU at the Applied Physics Laboratory in the University of Tsukuba, who has agreed to grow Ba/Si layers over our Ni/Si samples using his MBE device. First samples are deposition of Ba/Si over three NiSi substrates, the stoichiometric rates of Ba/Si are

changed from Ba-rich (10/46), normal (8/46) and Ba-poor (6/46) compositions. Therefore for the 10/46, 8/46 and 6/46 compositions the growth conditions are summarized in the table .2.

Second step consists of preparing other Ba/Si films on our Ni/Si substrates, therefore, ratios of Ba/Si=20/46 is considered. We successfully prepared four samples with Ni 100nm and four with Ni 150nm, eight in total. Each sample will be treated and measured separately. Growth parameters and condition for the Ba/Si=20/46 ratio are summarized in the table.3.

5.1. Rapid thermal annealing of samples

Now we have our samples with Si/Ni/SiO₂/BaSi/SiO₂ ready for annealing, according to our previous residual stress estimation in the nickel silicide, we will use the appropriate temperature/time condition to generate higher stress.

5.2. Thermal annealing of samples

This section summarizes our attempt to obtain clathrate thin film on silicon substrate. As illustrated in the figure, and as explained above, we aim to generate residual stress from nickel silicide formation (rapid heating/cooling) to induce the formation of Ba₈Si₄₆ clathrate phase.

Many experiments are done systematically, and characterizations are done through XRD and SEM techniques.

- 1- First samples were those with Ba/Si ratios of 6/46, 8/46 and 10/46, grown over NiSi substrates with 150nm thickness for Ni, and annealed at the same temperature/time conditions at 900°C/15minutes. Cooling time was 5 minutes.
- 2- Second samples are with extra barium Ba/Si=20/46, and were treated differently, hence, ten samples are prepared as follow:
For samples with nickel thickness of D_{Ni}=100nm, conditions are: 1) T=750°C, t=15 min.
2) T=800°C, t=10min. 3) T=850°C, t=10 min. 4) T=900°C, t=2min. 5) T=900°C, t=5 min.
6) T=900°C, t=10 min.
For samples with nickel thickness of 150 nm, conditions are: 1) T=750°C, t=15 min. 2) T=900°C, t=05 min. 3) T=900°C, t=10min. 4) T=900°C, t=15 min.
- 3- Third series of samples consists of two sample treated with the same temperature/time conditions, the first have 100 nm of nickel thickness and the second with 150 nm. Conditions are 880°C for 10 min, 5 minutes of rapid cooling.

6. Results and discussion

6.1. XRD

Firstly, we plotted the simulated XRD patterns for BaSi_2 , NiSi_2 , and $\text{Ba}_8\text{Si}_{46}$ type-I clathrate, in order to solicit them for comparisons. Figure 6 shows the simulated XRD patterns.

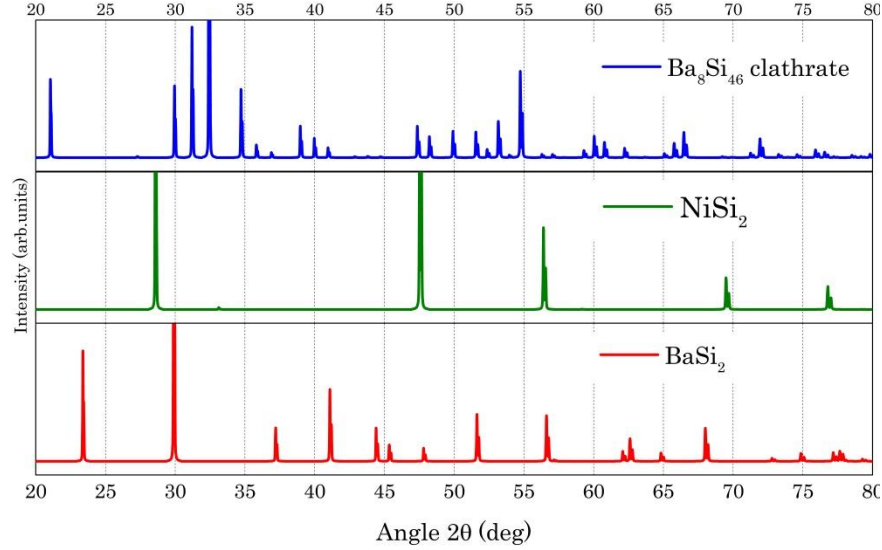


Figure.6. calculated XRD patterns for BaSi_2 , NiSi_2 and type-I $\text{Ba}_8\text{Si}_{46}$ clathrate.

First three samples: figure 7 shows the observed 2D-XRD patterns of the Ba/Si=6/46 and 10/46 samples treated at 900°C/15min. first analysis shows the peaks from NiSi_2 , Si substrate and small peaks of BaSi_2 . If we compare the two figures, we can observe that the peaks from Si(100) substrate is present simultaneously, whereas the peak from NiSi_2 at 48° is stronger in the 6/46 sample, and the other peaks at 57° and 62° are mainly from Ni/Si and stronger in the Ba/Si=10/46 sample. However, no barium is detected due to its evaporation after longue treatment time of 15 minutes. This can be solved by adding more barium and reducing the RTA time to 10 and 5 minutes, which will be done in the next steps.

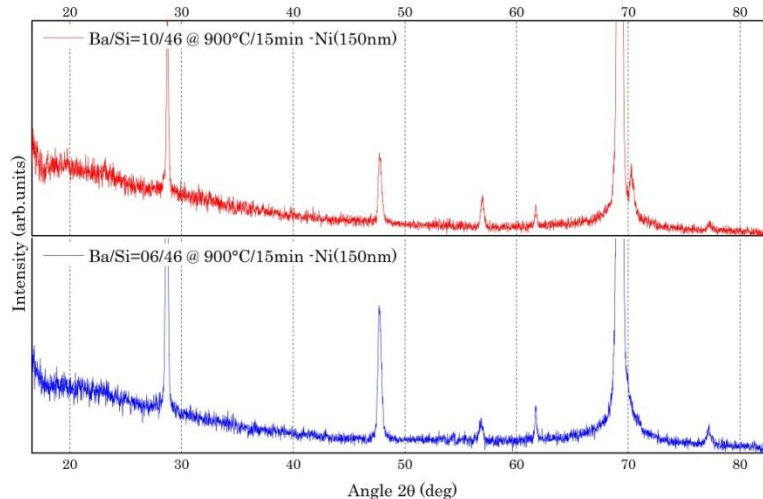


Figure.7. Observed XRD patterns for the first post-RTA samples.

Second samples: XRD patterns of the second set of samples with Ba/Si=20/46 annealed at 900°C/05 minutes are shown in the figure 8. In this figure, it can be seen that more peaks appears comparing to previous results. Those new peaks at 46°, 56° and 62° are from barium and BaSi₂ phase, beside the present NaSi₂ and Si as well. Ba peaks are more intense in the samples with Ni/150nm (we can assume that the thickness of Ni layer has some influence in the process, it generated more stress). However, no clathrate phases are detected.

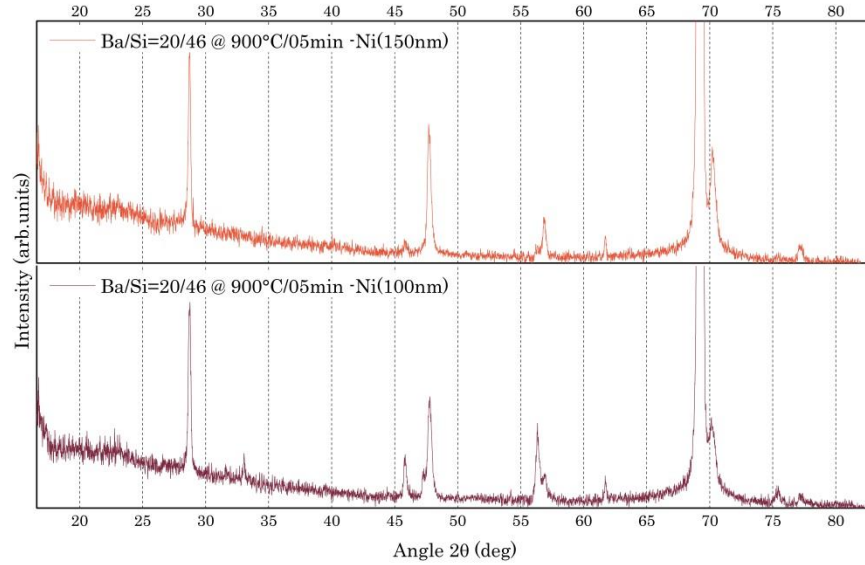


Figure.8. Observed XRD patterns for the second set of post-RTA samples.

Third set of samples: XRD pattern for the final set of samples annealed at 880°C/10min is illustrated in the figure 9. We notice strong peaks from NiSi₂, BaSi₂ and Si substrate as well. More barium is present in the samples with Ni/150nm, this confirms our assumption of the role of Ni thickness in slowing its evaporation.

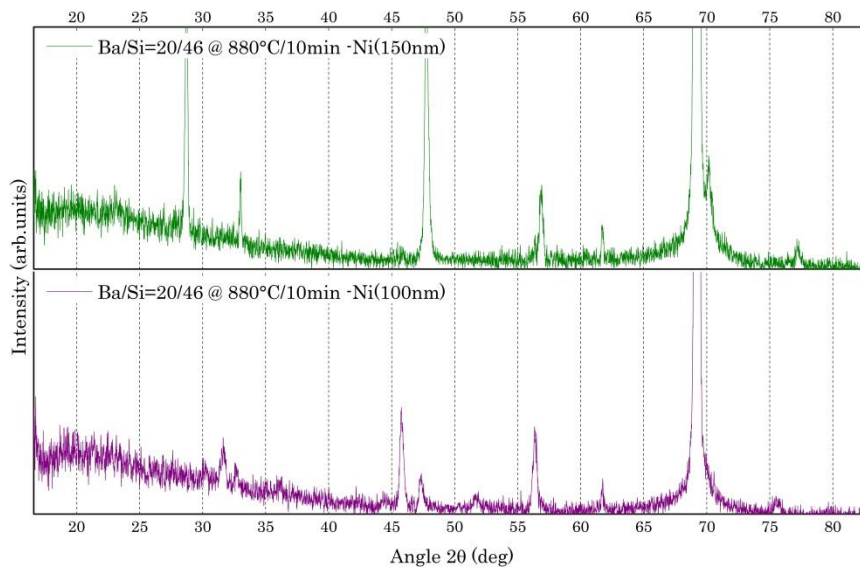


Figure.9. Observed XRD patterns for the third set of post-RTA samples.

7. Synthesis of quaternary silicon clathrate

The first synthesized sample has a chemical formula of: $K_8Ga_6Al_3Si_{38}$, for this aim a starting materials K (98% Sigma-Aldrich), Ga (99.99% Furuuchi chemicals), Al (99.99% Furuuchi chemicals) and Si (6N=99.9999% Furuuchi chemicals) were weighted following a 10:6:3:38 molar mixture ratios. The mixture was loaded into a BN capsule and then sealed in a SS tube in a glove-box; the SS tube is then heated to 1244 K (970°C) for 24 hours and then cooled naturally. A total mass of 2.2g will be synthesized, for that purpose our starting raw materials are weighted following the formulas below:

- K_{10} : $39.09 * 10 = 390.9$
- Ga_6 : $69.74 * 6 = 418.44$
- Al_3 : $26.58 * 3 = 79.74$
- Si_{38} : $28.09 * 38 = 1067.42$
- $Total = 1956.5$

$$mK = (390.9 * 2.2) / 1956.5 = \mathbf{0.44\text{ g}}$$

$$mGa = (418.44 * 2.2) / 1956.5 = \mathbf{0.47\text{ g}}$$

$$mAl = (79.74 * 2.2) / 1956.5 = \mathbf{0.09\text{ g}}$$

$$mSi = (1067.42 * 2.2) / 1956.5 = \mathbf{1.2\text{ g}}$$

$$Total = 0.44 + 0.47 + 0.09 + 1.2 = \mathbf{2.2\text{ g}}$$

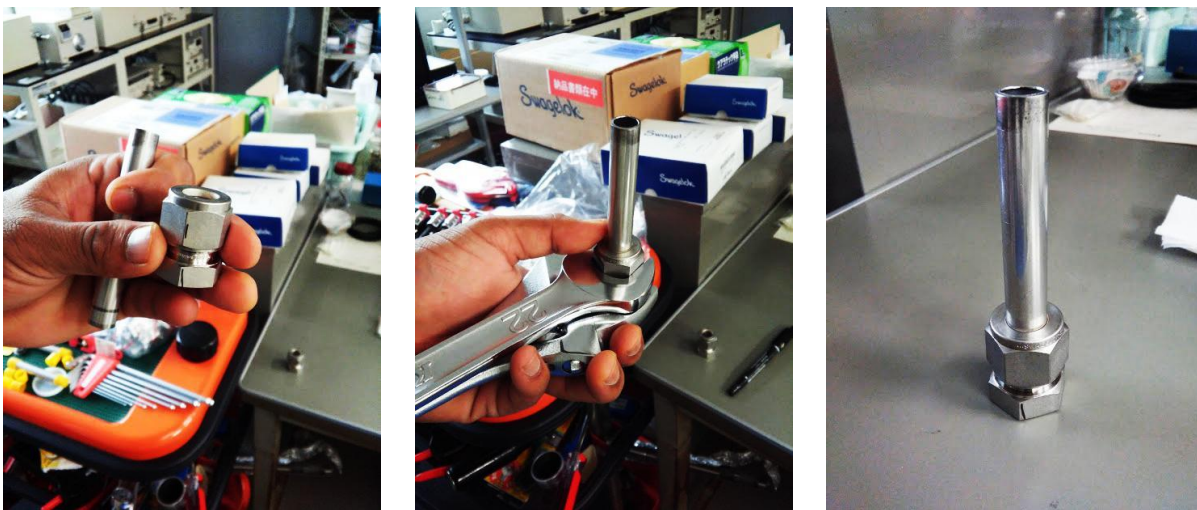


Figure.1: Preparation of stainless steel tubes.

The obtained sample will be mixed another time and grinded manually inside the glove-box using a marble mortar, and sealed in a BN capsule and in an SS tube and heated again under 970°C in order to get a homogenous composition.

Preparation and weighting of starting raw materials:

Gallium (pieces) is weighted outside the glove-box, while the other materials (Silicon powder, Aluminum powder and potassium chunks) are prepared inside the glove-box. Extra weight will be taken for Ga and Al. The materials are well mixed in the glove-box using a mortar.



Figure.2: Preparation and weighting of potassium (left) and silicon (right).



Figure.3: MIWA Glove-box.

After preparing the starting materials and sealing them into a stainless steel tube, we will put the tube inside a regular furnace programmed to reach a 970°C temperature within 24 hours and then to cool down naturally for 12 hours the whole operation will take about 36 hours in total.



Figure.4: heating process.

From this process we have obtained 2.2 g of our material (supposed $K_8Ga_6Al_3Si_{38}$) but we are not sure about its real composition. We will make another melting process using the same procedures as above.

After the synthesis, characterization must be carried on in order to reveal different properties of the material in question, which will be done in the following weeks. It will include: Xray-diffraction, Rietveld refinement, Neutron-diffraction, Scanning Electron microscopy, Density measurement, transport measurement, Optical measurements. The binary clathrate Ba_8Si_{46} will also be synthesized (bulk) by mean of the arc melting process so it will be used as target material for future clathrate thin-film elaboration.

The next step consisted (upon the work plan) to synthesize the type-I Ba_8Si_{46} binary clathrate using the arc-melting technic. We prepared and weighted the starting materials with the corresponding quantities and operated the arc-melting process. I have attended this operation.

8. Experimental details

We have 1.64767g of barium and 1.9371g of silicon; these weights correspond to a molar mixture of 8:46, and a total weight of 3.539g. The raw materials are put into the water-cooled copper crucible inside the vacuum chamber of the arc-melter; in another crucible a piece of titanium is put. The latter is used as an oxygen absorber, when melted it will react with the

oxygen atoms in the chamber and form titanium oxide. Then the barium is melted in order to get rid of the oxide on its surface, and after it cools down it will be moved to the same crucible with silicon and melted together, this last step will be repeated at least four times for sake of homogenization. The as-synthesized sample (see figure 1), is cut and a part is grounded using a marble mortar. Powder X-ray diffraction XRD is carried out using a RIGAKU diffractometer operating at 40Kv and 150mA with a copper source $\text{CuK}\alpha$ (wavelength=1.5405 Å) of x-rays. We have obtained the pattern depicted in figure 2(a). We will first analyze and compare this pattern with simulated patterns of BaSi_2 , Si and $\text{Ba}_8\text{Si}_{46}$, respectively; the three patterns are obtained using crystalline structures generated from published ‘CIF files [1,2,3]’, we used the REFLEX module within the Materials Studio package for this purpose (generating crystalline structures and their respective XRD patterns) [4].



Figure.1: Arc-melted Ba:Si with molar mixture of 8:46

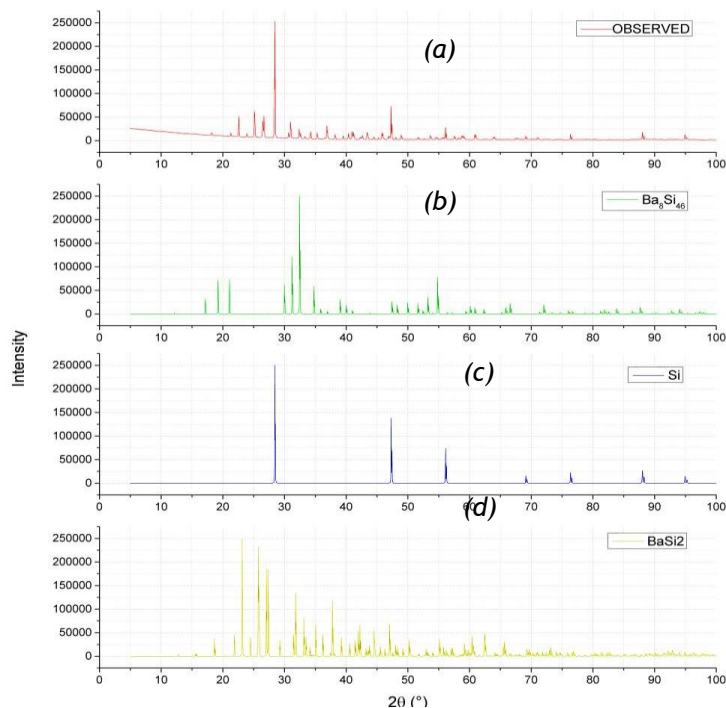


Figure.2: XRD patterns of the synthesized (a), BaSi_2 (b), Si (c), and $\text{Ba}_8\text{Si}_{46}$

Figure.1 shows the synthesized sample. Figure.2 illustrates the powder X-ray diffraction patterns (intensity versus the angle 2θ) of the as-synthesized material (a) in comparison with the theoretical patterns (b,c,d). It can be noticed that all the peaks in our synthesized samples come from the combination of Si and BaSi₂ peaks, and **none clathrate** peak is formed though; our material is a mixture of Si and BaSi₂ phases only.

The BaSi₂ is known to be a very stable material under high temperatures, which is why we couldn't obtain a clathrate phase with arc-melting technic, to do so the High Pressure High Temperature HPHT technique must be solicited. High pressure is needed to transform the BaSi₂ phase and high temperature to fuse it with extra silicon to achieve the desired clathrate formula [5].

Remark: It is very important to report that alkaline earth metals (Be, Mg, Ca, Sr, Ba, and Ra) and alkali metals (Li, Na, K, Rb, Cs, Fr) are highly reactive elements, they tend to react with oxygen and atmospheric moisture when exposed to air, and are very toxic by ingestion and hazardous, it is then indispensable for the operator to check the so called: “Materials Safety Data Sheet: MSDS”. Each element in the periodic table has its own safety data sheet, whether in electronic (pdf) or printed form delivered by the material's manufacturer. However, it is then highly recommended to handle these elements under an inert gas atmosphere (glove-box), and to store them under oil in order to prevent their reaction.

The synthesis of ternary clathrate with formula: Ba₈Al_xSi_{46-x} using the arc-melting method (we took $x=10$). For that purpose, the starting materials are weighted for a molar mixture of 8:10:46. The starting weights are 1.26319g, 0.31g and 1.1625g for Ba, Al and Si respectively.

Following the same steps as described above. The as-synthesized sample is cut to four parts using a slow speed circular saw. One thin part is grounded and prepared for powder X-ray diffraction analysis. Another part is also prepared for future transport measurements.

Figure.3 shows the obtained powder XRD patterns for our synthesized material compared with the Ba₈Al_{6.9}Si_{39.1} generated from a CIF file from reference [6]. It is noticeable that the two patterns have similar allures; intensity peaks appear at the same angles.

We can say that a type-I clathrate phase is obtained, however, for deep insight of the structural properties of our material, further analysis of the pattern must be held including as first step the indexation and then refinement. An appropriate indexation will provide relevant

information such as miller planes indices (h, k, l) and lattice parameters, while a refinement procedure is necessary to obtain more details such as atomic positions, bonds lengths, etc.

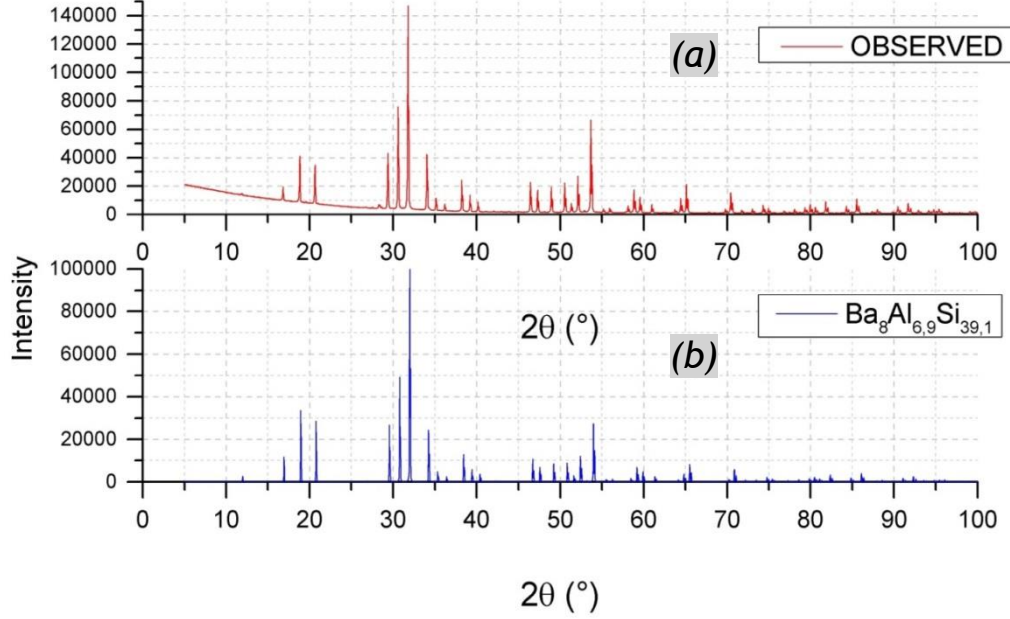


Figure.3: Powder XRD patterns of the synthesized (a) and the $Ba_8Al_{6.9}Si_{39.1}$ [61] (b).

After synthesizing various type-I silicon clathrates i.e.: $(K_8Ga_{8-x}Al_xSi_{46})$ and $(Ba_8Al_xSi_{46-x})$, with two different techniques (thermal melting and arc melting respectively), powder x-ray diffraction patterns (PXRD) are collected and refined in order to get necessary structural information. Also, thermal properties measurements are carried out along with other measurements.

8. X-ray powder diffraction

As detailed in the second report (2nd week report Dec, 7th to Dec, 13th), we successfully synthesized the $Ba_8Al_{10}Si_{36}$ using arc-melting, we showed (after comparison with calculated pattern for $Ba_8Al_{10}Si_{36}$ from literature) that a type-I clathrate phase is formed. The collected PXRD pattern will undergo indexation and then refinement operations, for indexation the REFLEX module included in the Materials studio package will be used, and for refinement, the Fullprof software is used.

1. PXRD pattern indexation:

The powder XRD pattern of our synthesized sample $\text{Ba}_8\text{Al}_{10}\text{Si}_{36}$ obtained from the Rigaku diffractometer is illustrated in Figure.1 and it was indexed using the REFLEX module within the Materials Studio Package. The reflex module contains many sub-modules each one is conceived for a particular task: pattern processing, powder diffraction, powder indexing, powder refinement, powder cristallinity, powder QPA, and powder solve, it is then a powerful and complete package for powder x-ray studies and analysis. We will use the powder indexing firstly.

Figure.1 shows our obtained PXRD pattern from the Rigaku diffractometer, we operated the device under 40KV, 150 mA power, x-ray is generated from a $\text{Cu}(\text{k}\alpha)$ source ($\lambda = 1.5406$ Å).

In this report, the primary structural properties of our arc-melted sample ($\text{Ba}_8\text{Al}_{10}\text{Si}_{36}$) are investigated by analyzing its powder XRD pattern using the Rietveld method within the Fullprof software.

The powder XRD pattern of our synthesized sample $\text{Ba}_8\text{Al}_{10}\text{Si}_{36}$ obtained from the Rigaku diffractometer is illustrated in Figure.1 and it was indexed using the REFLEX module within the Materials Studio Package. The reflex module contains many sub-modules each one is conceived for a particular task: pattern processing, powder diffraction, powder indexing, powder refinement, powder cristallinity, powder QPA, and powder solve, it is then a powerful and complete package for powder x-ray studies and analysis. We will use the powder indexing firstly.

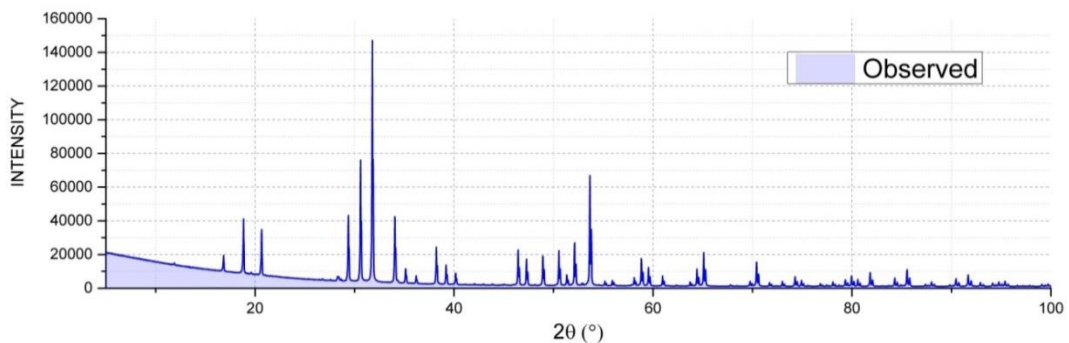


Figure. 1: Observed powder XRD pattern of the synthesized $\text{Ba}_8\text{Al}_{10}\text{Si}_{36}$ sample.

In order to index any powder XRD pattern, many steps must be followed carefully to obtain required structural information, including: 1) identification of the pattern peaks (searching the

positions of each peak), 2) identification of phases, 3) comparison of the observed pattern with the expected one, 4) picking up the desired peaks (get rid of undesirable phases), 5) indexing the remaining peaks, 6) obtaining Miller indices (h,k,l), and finally 7) getting the lattice parameters and angles.

Table.1: structural properties obtained from first indexation of the pattern ($Ba_8Al_{10}Si_{46}$)				
Parameter	a (Å)	b (Å)	c (Å)	α ° β ° γ °
Cubic	10.51916	10.51916	10.51916	90°
Orthorhombic	10.51523	7.43933	4.90578	/

Table.1 shows the results of powder XRD pattern indexation. The DICVOL91 software included in the Pattern Indexing sub-module is used for that purpose, we searched for cubic, tetragonal, hexagonal and orthorhombic solutions, no solutions were found for tetragonal and hexagonal systems but only for the cubic and orthorhombic systems. 18 peaks are identified in the experimental pattern, for each peak miller indices are attributed from the cubic system resolution (Figure.2), the DICVOL output files for the cubic and orthorhombic systems are given in annexes (a) and (b) respectively.

These results will undergo further refinement.

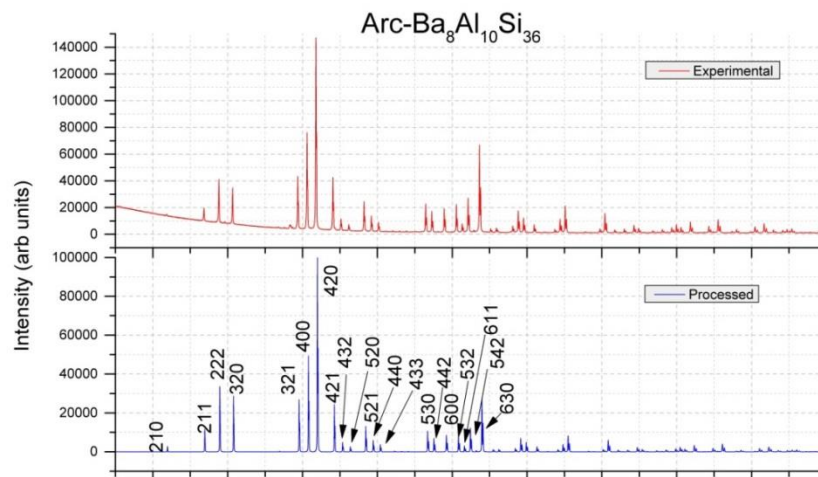


Figure.2: Experimental powder XRD pattern (a) and the processed pattern (b) with corresponding Miller hkl indices for the first 20 peaks obtained from DICVOL91 indexing process.

9. Powder XRD refinement:

For that purpose, we will solicit the Fullprof software. The Rietveld refinement is used with the 'Least squares' as refinement weighting method; peak shapes are modeled by mean of the 'Pseudo-Voigt function', the number of refined parameter is 15 (including: lattice parameters and angles, atomic positions, atomic occupancies), all atoms are the background was defined using the WinPlotr block where 68 refined points are considered. The final refinement fitting and difference is illustrated in figure.2, after several operations of refinement, the difference coefficient $CHI2$ was fixed at $X^2=32.4$ (the minimum value we could obtain), the final yielded structural results are listed in table.2.

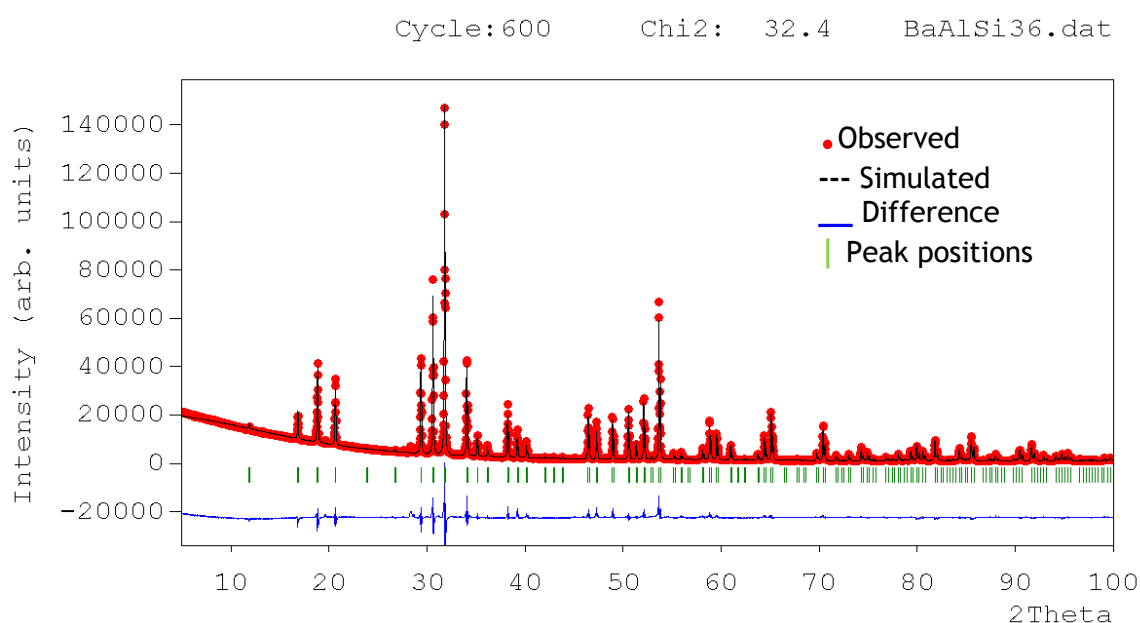


Figure.3: Rietveld refined powder XRD pattern of the synthesized $Ba_8Al_{10}Si_{36}$ sample, experimental intensity (red dots), calculated intensity (black line), calculated peak positions (green lines) and the difference curve (blue line).

From Rietveld refinement, a chemical formula of $Ba_{7.6}Al_9Si_{37.08}$ with type-I clathrate (Pm-3n) space group is confirmed. The filling percentage is 95%, 90% and 90.95% for Ba, Al and Si respectively. An extra amount of silicon is found, it indicates the presence of Si phases (will be confirmed later), and Ba deficiency can be attributed to its evaporation during the melting process. Figure.3 shows the crystalline structure generated from Rietveld refinement (CIF file).

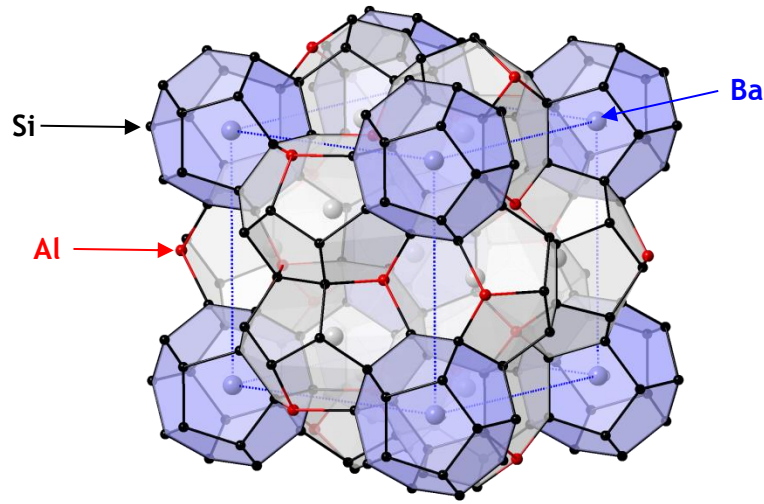


Figure.4: Crystalline structure of the $Ba_8Al_{10}Si_{36}$ generated from CIF file from refinement process.

Composition	$Ba_{7.6}Al_9Si_{37.08}$
Crystal system	Cubic
Space group (number)	$Pm-3n$ (n° 223)
Lattice parameter ($\text{\AA}$)	10.519365
Atomic positions (site occupancy)	(x , y , z)
Ba1(2a) (1.98)	(0.0 , 0.0 , 0.0)
Ba2(6d) (5.66)	(0.25 , 0.5 , 0.0)
Si1(6c) (3.61)	(0.25 , 0.0 , 0.5)
Si2(16i) (15.61)	(0.18515 , 0.18515 , 0.18515)
Si3(24k) (22.61884)	(0.0 , 0.30255 , 0.11754)
Al1(6c) (4.30)	(0.25 , 0.0 , 0.5)
Al2(16i) (2.73)	(0.181515 , 0.181515 , 0.181515)
Al3(24k) (1.97158)	(0.0 , 0.30255 , 0.11754)

10. Physical properties measurements

After knowing that our synthesized material is mostly composed from the type-I clathrate phase, its physical properties have to be investigated in order to get further information on whether it is a metal or a semiconductor and also to identify its thermoelectric potentials. For

that purpose physical properties measurements system PPMS by Quantum Design will be used, the thermal transport option TTO for measuring thermoelectric properties is held using the four probe method, Thermal conductivity, Seebeck coefficient, Electrical resistivity and the thermoelectric Figure of merit are all measured within the system. The electrical resistivity is reported firstly, the other three properties are meant to be seen along with other measurements such as the Hall coefficient and voltage and carrier mobility and density (next report if possible).

The most common way for measuring the resistivity of a material is the four-point probe technique, it consists of making equally spaced probes in contact with the material, the two outer probes are used for sourcing current, while the two other contacts are used for measuring the resulting voltage, (see Fig.3), hence, the volume of the investigated sample must be precisely known in order to quantify resistivity's value according to the formula.1. The sample was cut and the 4 contacts were made with a golden thin wires and gold epoxy and then mounted on the PPMS sample puck (as shown In Fig.5).

For measuring the resistivity, three excitation currents are used, and the temperature is varied in the range between 0 and 300K, we will obtain resistivity versus temperature plot for each selected current. See figure.6. ((a) $I_1=0.1\text{mA}$, (b) $I_2=1\text{mA}$ and (c) $I_3=10\text{mA}$).

From Figure.6 it can be concluded that our material is metallic, no semiconducting behavior is noticed though.

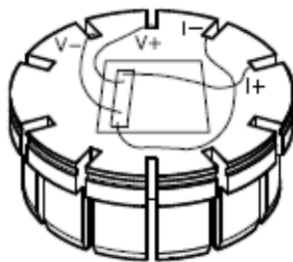


Figure.5: Example of four-wire resistance measurement with sample mounted on standard PPMS sample puck.

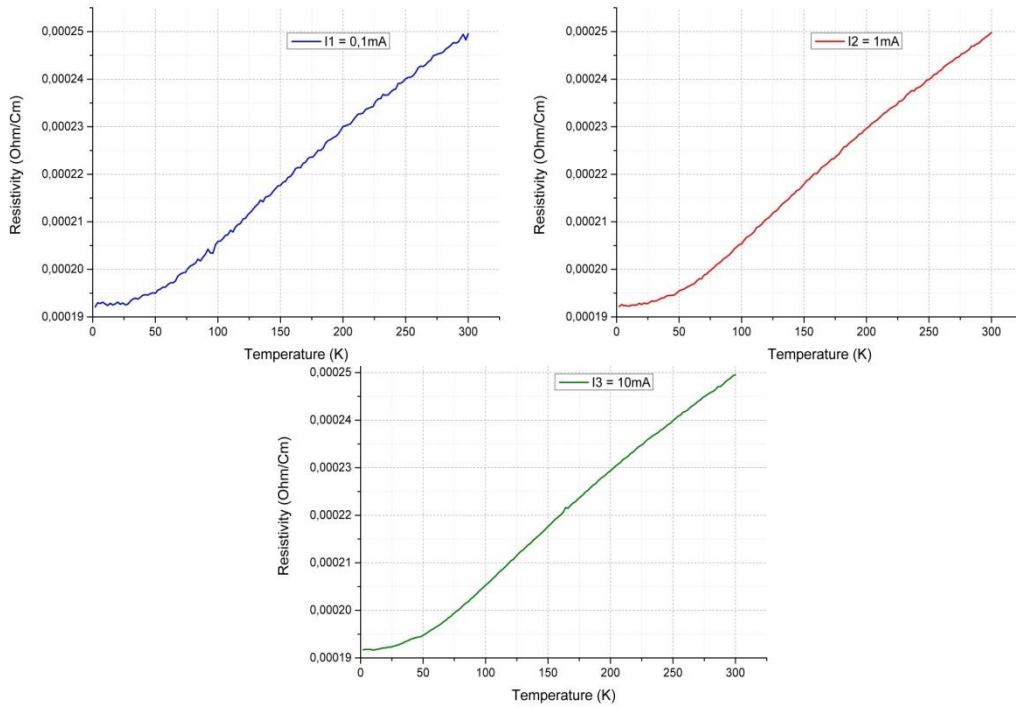


Figure.6: Electrical resistivity as a function of the temperature for the arc-synthesized $Ba_8Al_{10}Si_{46}$ sample.

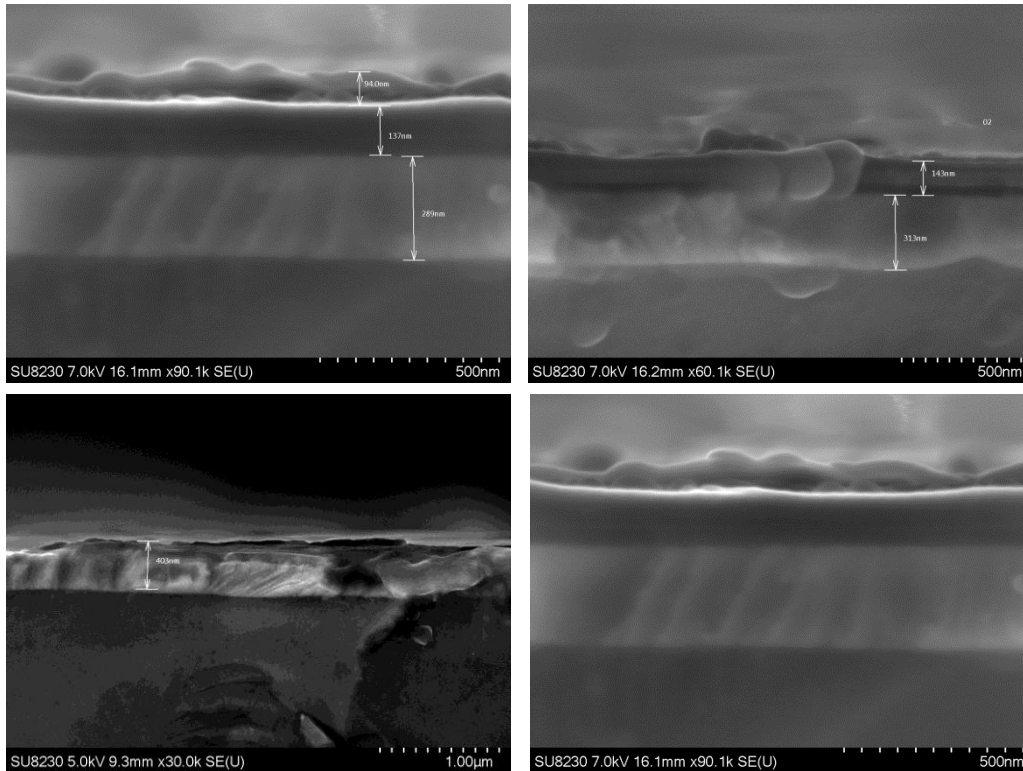


Figure.7: Thin films of NiSi/BaSi over Si(001) and Si(111) substrates by Scanning electron microscope.

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General Conclusion & Perspectives

General Conclusion & Perspectives

The aim of this thesis was to investigate the physical properties of some silicon clathrate materials and to engineer their properties in order to obtain a direct bandgap material that will be candidate for future solar cell or optoelectronic devices. Starting with calculating through first-principles tools their fundamental properties such as structural, electronic and optical properties. Along this study, two major codes based on the pseudopotential approach within the density functional theory framework were solicited, including CASTEP and DMO³, both available within the Materials Studio package. From these codes two distinct functionals were used, i.e. the GGA-PBE and the hybrid BLYP functional, and results were compared. We noted the following:

Our calculation for the guest containing clathrates of the type-I structure (X_8Si_{46} , $X = Ca, Ba, Na, K, Cs$ and Rb) has shown that these materials have similar band structures and differ in the Fermi level, which was confirmed that they obey to the “rigid band structure” rule, which is common characteristic of all cage-like structures.

The guest-free silicon clathrate Si_{46} in its two phases (type-I and type-VIII) is a semiconductor with a quasi-direct bandgap in the optimum value of the visible range of the electromagnetic spectrum, very promising for photovoltaics or optoelectronics applications.

They can be engineered towards direct bandgap materials through biaxial strain for example, and that was the original result to be published in our first paper.

The BLYP approximation revealed better results for the bandgap magnitude for both materials.

Deep investigation of the optical transition in both materials showed a possible optically active transition in the type-VIII Si_{46} , whereas no active transition was observed in its type-I counterpart. This was done by two methods in order to get similar and confident results (manually and through Quantum Espresso code). These original results were published in our third paper included here after.

Results obtained throughout this part were coherent and in a very good agreement with those available in the literature. This encouraged us to publish and communicate our works.

Experimental work was done alongside with the theoretical work; the main objectives here were to first get familiar with different synthesis and characterization techniques, and to handle the synthesis of some silicon clathrates. Therefore, visits to Sweden and Japan allowed me to gain such a great amount of experimental skills. We successfully synthesized quaternary and ternary bulk clathrates in the type-I, and our project to elaborate thin films of the type-I clathrate are still on the run, we have to mention that this is a very challenging task that requires many experiments.

As perspectives,

In order to better understand the physics and chemistry of silicon clathrates, tough and deep amount of research must be achieved on both theoretical and experimental fronts.

I hope to pursue my future research on this class of materials that is still revealing intriguing properties.

Future plans also include the conception of a complete Si clathrate-based solar cell. PN junction must be well conceived and appropriate p-type and n-type clathrates will be obtained through what is known as intrinsic doping by guest atoms.

Finally, I hope that the work realized along this journey will allow the opening of new perspectives to the exploration and exploitation of the interesting properties these materials have exhibited along, and I hope that our results will be useful to complete and to enhance the performances of future generation of all-silicon solar cells and optoelectronic devices.

List of publications

List of Publications

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List date: March 4th, 2018

Peer-reviewed scientific articles:

- Nassim Ahmed Mahammedi, Marhoun Ferhat, and Rachid Belkada: **Prediction of indirect to direct band gap transition under tensile biaxial strain in type-I guest-free silicon clathrate Si₄₆: A first-principles approach: Superlattices and Microstructures, Volume 100, December 2016, Pages 296-305.**
- Nassim Ahmed Mahammedi, Marhoun Ferhat, and Rachid Belkada: **A Comparative Study of the Effect of Strain on the Electronic and Optical Properties of Filled and Unfilled Ba₈Si₄₆ Type I-Clathrate: Acta Physica Polonica A. Nov 2017.**
- Nassim Ahmed Mahammedi, Marhoun Ferhat, Takao Tsumuraya and Toyohiro Chikyow: **Prediction of optically-active transitions in the type-VIII guest-free silicon clathrate Si₄₆: a comparative study of its physical properties with the type-I counterpart through first-principles. JOURNAL OF APPLIED PHYSICS 122, 205103 (2017), November 2017.**

Conferences proceedings:

- **2014:** Materials Study Days (**Journées d'études sur les matériaux JEM'14**): **April 14-15, University Amar Têlidji of Laghouat, ALGERIA.** (Organizer, Oral presentation & Poster: *Silicon clathrates, potential materials for energy conversion applications*)
- **2015:** International Conference on Substantial Environmental Engineering and Renewable Energy (**SEERE-15**) on **13-14 January 2015, Abu Dhabi (UAE).** (Poster: bandgap engineering of silicon clathrates)
- **2015:** Algerian Japanese environment and energy workshop, **30-31st March 2015, National Institute for Material Science (NIMS), Tsukuba-JAPAN.** (Workshop & head to head meetings)
- **2016:** 3rd International conference on computational and experimental science and engineering (**ICCESEN-2016**) **19-24 October 2016, Antalya-TURKEY.** (Accepted paper:

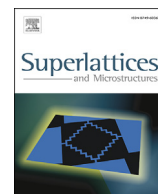
A Comparative Study of the Effect of Strain on the Electronic and Optical Properties of Filled and Unfilled Ba₈Si₄₆ Type I-clathrate)

- **2017:** International Conference on Engineering, Science, and Application (**ICESA-2017**). **16-18 August 2017, Tokyo-JAPAN.** (Oral presentation & Poster: *Strain induced bandgap-engineering of Silicon clathrates: Towards a direct bandgap silicon for future solar cells*).

Dissertations:

- **Present: PhD student:** Electrical engineering, PHOTOVOLTAIC PHYSICS, Thesis title: *"Silicon Clathrates, Potential Materials for Energy Conversion Applications"*. Graduation date: June 2018
- **2012: Master' Degree (Magister)** in PHOTOVOLTAIC PHYSICS, Memoir title: *"First-principles Studies of intrinsic point defects in Cu-III-S₂ chalcopyrite materials"*. Mai 31st 2012
- 2009: State Electronics Engineer,** Majored in: INSTRUMENTATION, Memoir title: *"Numerical Simulation of a Cu (In, Ga) Se₂ solar cell"*. June 15th 2009

Important Papers



Prediction of indirect to direct band gap transition under tensile biaxial strain in type-I guest-free silicon clathrate Si₄₆: A first-principles approach



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ARTICLE INFO

Article history:

Received 27 June 2016

Received in revised form 19 September 2016

Accepted 26 September 2016

Available online 28 September 2016

Keywords:

First-principles calculations

Silicon clathrates

Biaxial strain

Direct bandgap

ABSTRACT

We suggest a bandgap engineering approach of first-principles calculations on basis of density functional theory (DFT), to monitor the bandgap transition from indirect to direct for the type-I guest-free silicon clathrate (Si₄₆). Hence, we have systematically investigated the effect of planar biaxial strain in either compressive or tensile directions on electronic and optical properties using both GGA-PBE and hybrid GGA-BLYP functionals as implemented in Castep and Dmol³ codes respectively. For unstrained Si₄₆, electronic structure has revealed a semiconducting behavior with quasi-direct bandgap estimated at 1.364eV (GGA-PBE) and 1.618eV (GGA-BLYP). Thus, we predict that tensile biaxial strain above +2% can trigger the indirect to direct bandgap transition, which will be located at the X(1/2,0,0) high symmetry point in the first Brillouin zone. The bandgap magnitude increases with the decreasing of biaxial strain and reaches a maximum value of 1.406eV (GGA-PBE) and 1.641eV (GGA-BLYP) at +1% tensile strain, and starts to decrease toward smaller values when the strain is increased. In addition, some relevant optical properties such as the complex dielectric function and the absorption coefficient are computed at each step of biaxial strain. Under tensile strain of +4%, results show better optical properties, the general magnitude of the absorption spectrum is increased by 17.5% with a maximum magnitude of 2.7×10^4 in the visible range of the electromagnetic spectrum.

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1. Introduction

Beside its leading status as key material in microelectronics and optoelectronics, silicon thrones the photovoltaic market by a dominative share. This leading position is actually due to its many advantages, it is the second most abundant substance on the earth's crust after oxygen (presenting about 25.8% earth's global mass), it has a very stable and excellent oxide SiO₂ [1], its physical-chemical properties are well established and mastered at both research and industrial levels. However, its development as a strategic material for photovoltaics is permanently challenged by its shortage related to the indirect nature of its bandgap, which means that an excited electron in valence band requires a change in its momentum to leap to conduction band by an intervention of a phonon in the bulk. In consequence, this makes silicon a very weak light absorber, the

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thickness of the absorber layer must be at least equal or superior to the mean-free path of charge carriers to skip the recombination phenomena in the bulk, making the first-generation solar cells of silicon relatively thick (about 200 μm) [2]. In order to overcome this problem, the research society came with many innovative and diverse solutions, such as predicting semiconductors with direct bandgaps, as for the case of III-V (GaAs) [3], Chalcopyrites CIGS [4] and cadmium telluride CdTe [5] which already have revealed promising high efficiencies. So far the wide development and mass production of these materials is limited as they use expensive and rare precursor elements such as indium, gallium, and sometimes toxic as arsenic, selenium and cadmium. An ideal solution would be to keep silicon as the main material, and try to engineer its atomic structure to get desired properties [6]. In this context, other allotropic forms of silicon are explored and have exhibited promising physical-chemical properties that could be used in energy conversion systems. Depending on their atomic arrangement and their method of synthesis different forms of silicon-based compounds are obtained. The second known crystalline form after diamond is the cage-like structures named 'Clathrate'. Clathrates are crystalline inclusion compounds in which the cage formed by host atoms (group IV: C, Si, Ge) encloses within guest atoms or molecules (mostly alkali metal, rare earth or alkaline atoms), [7]. Inspired from hydrate clathrates, their main framework structure consists of face-sharing polyhedrons whose are directly responsible for defining the clathrate's type. Since their synthetize in 1965 by two French groups Kasper et al. [8] and Cros et al. [9], group-IV clathrates due to their exceptional thermoelectric [10,11] and superconductive [12,13] properties, have encountered a great amount of experimental and theoretical investigations. Recently, this class of material has attracted more attention as candidate for photovoltaic applications, [6,14]. Type-I Silicon clathrate with chemical formula $X_8\text{Si}_{46}$ where X is the guest atom, is the most studied clathrate among the other types, its properties are under investigations and are still revealing more new features, it has been synthetized through a diversity of technics such as arc-melting [15] or high pressure high temperature synthesis HPHT [16,17]. More recently, thin film based on clathrates including sodium doped silicon clathrates in type-I $\text{Na}_8\text{Si}_{46}$ and type-II $\text{Na}_x\text{Si}_{138}$ [18]. Germanium-gallium clathrates with the chemical formula of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ are successfully grown [19]. An attempt to grow a guest-free Si_{46} silicon clathrate was reported [20], and lately a successful growth of thin film of 1 μm of type-II guest free silicon clathrate Si_{136} over a (111) Si substrate by thermal decomposition of NaSi precursor films and Na removal from the $\text{Na}_x\text{Si}_{136}$ film by a heat treatment with iodine [21].

In the present study, we aim to establish conditions to obtain direct bandgap silicon that can be useful to achieve better efficiencies for solar cells. To the best of our knowledge, strain technology is a well-known and practical technique used to engineer bandgap of semiconductors, it has been applied to improve performances of structures and devices based on diamond silicon [22–24], however, this technique has not been yet used to tune silicon clathrates properties. With this motivation, we have systematically investigated the impact of the in-plane compressive and tensile biaxial strains on the structural, electronic and optical properties of hypothetical guest-free type-I silicon clathrate Si_{46} by means of first-principles calculation within the DFT approach.

2. Theoretical approach

2.1. Computational details

In this work, our first-principles calculations based on the density functional theory DFT [25,26] are carried out by CASTEP (Cambridge Serial Total Energy Package) [27] and Dmol³ [28] codes. In order to solve the Kohn-Sham equations of the DFT, Ultrasoft pseudopotentials of Vanderbilt-model included in the Castep package were employed in real space [29]. The exchange and correlation energy (XC) was treated within generalized gradient approximation (GGA) using the Perdew-Burke-Erzenhorr PBE parameterization [30], this choice is justified by the fact that GGA-PBE functionals has revealed better convergence of the total energy, the ionization energy and the Si–Si bonds lengths and angles for silicon based compounds compared with the local density approximation (LDA) [31]. By means of a self-consistent-field (SCF) calculations, under criterion for the convergence of the total energy of 5.10^{-4} eV/atom and 0.001 GPa for pressure, the plane-wave cutoff-energy was set to 480 eV, while the first irreducible Brillouin zone in the reciprocal space was sampled at a $6 \times 6 \times 6$ grid using the Monkhorst-Pack scheme [32]. In order to minimize the total energy of the system, geometrical and internal coordinates were rigorously relaxed until obtaining 'Hellmann–Feynman' interatomic forces lower than 10^{-3} eV/Å, this task was accomplished using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) optimization algorithm [33–36]. For the relaxed configuration, major optical properties were computed for each step of biaxial strain. However, for the calculation of the optical spectra of the dielectric function a dense set of k-points sampling in the Brillouin zone are adopted using $14 \times 14 \times 14$ grid of Monkhorst-Pack scheme, which is highly recommended for calculation of optical properties [37]. Hybrid GGA-BLYP [38,39] functional was solicited through Dmol³ code [28] to recalculate band structures for optimized structures in order to improve bandgap magnitudes as they are expected to be underestimated by regular GGA-PBE functional. For that purpose, the Brillouin zone was sampled into a grid of $10 \times 10 \times 10$ using Monkhorst scheme giving 75 k-points.

2.2. Structural aspects

Type-I guest-free silicon clathrate Si_{46} crystallize in the simple cubic space group $Pm\bar{3}n$ (number 223) [40]. Its unit cell contains 46 atoms, is formed by assembly of eight face-shared elemental cages: two dodecahedral Si_{20} (twelve pentagonal faces with 20 atoms) and six tetrakaidecahedral cages Si_{24} (twelve pentagonal faces and two hexagonal faces with 24 atoms) [40,41], the vacant cavities within the cages are often filled with guest atoms or molecules. In the present study, the initial

lattice is built from crystalline parameters taken from Ref. [42] ($a = 10.055 \text{ \AA}$), then optimized along with internal atomic coordinates to reach the equilibrium state. At minimum of total energy and interatomic forces, our optimal internal atomic coordinates (following the Wyckoff notation) and lattice parameters are in a good agreement with previous HF-LCCO [43], LDA [44,45], GGA [46], TBTEMD [42], GTBMD [47] and LDA [48] calculations. Table 1 summarizes our results in comparison with the literature. Fig. 1(a) shows a unit cell of X_8Si_{46} including the Wyckoff positions. Fig. 1(b) illustrates the two initial polyhedrons forming the Si_{46} main framework of the lattice. To the best of our knowledge, experimental values for guest-free type-I Si_{46} are not reported so far, therefore, we took experimental values of Na_8Si_{46} as a reference structure [49] ($a = 10.19 \text{ \AA}$) to be compared with. This choice is justified as that due to relative large size of silicon frame-work cages, which is less affected by the presence of guest Na atom where the small atomic radius of Na induces no volume increase in the structural transition between Si_{46} and Na_8Si_{46} lattices according to [44]. As regard to the mechanical properties, the cubic nature of clathrate leads to define only three independent elastic constants which are given for type-I clathrate Si_{46} as: $C_{11} = 155,140,135 \text{ GPa}$, $C_{12} = 65,47,58 \text{ GPa}$, and $C_{44} = 45,47,40 \text{ GPa}$, the density is $\rho = 2.1, 2.098, 2.05 \text{ g/cm}^3$ as all respectively reported by Refs. [42,50,51]. We report a density of $\rho = 2.01 \text{ g/cm}^3$.

2.3. II.3. Biaxial strain simulation

The biaxial strain is applied by imposing a biaxial stress tensor ($\sigma_{11} = \sigma_{22} \neq \sigma_{33}$) on the material where the same amount of stress is applied along the $\langle 100 \rangle$ and $\langle 010 \rangle$ directions $\sigma_{11} = \sigma_{22} \neq 0$ and the out-of-plane axis along $\langle 001 \rangle$ direction is free of stress $\sigma_{33} = 0$. The strain tensor can be determined through the Hooke's laws of general elasticity [53–55].

$$(\sigma_{ij}) = (C_{ij}) (\varepsilon_{ij}), \quad i, j = 1, 2, 3 \quad (1)$$

In order to simulate both compressive ($\varepsilon_{11} = \varepsilon_{22} < 0$) and tensile ($\varepsilon_{11} = \varepsilon_{22} > 0$) in-plane biaxial strains that any epitaxial thin film undergoes when it is grown over substrates with different lattice constants, the lattice parameters at the equilibrium state are modified according to Formulas (2) and (3),

$$\varepsilon_{11} = \varepsilon_{22} = \frac{a - a_0}{a_0} = \frac{\Delta a}{a_0} \quad (2)$$

$$\varepsilon_{33} = \frac{c - c_0}{c_0} = \frac{\Delta c}{c_0} \quad (3)$$

where: ($\varepsilon_{11}(\%) = \varepsilon_{22}(\%)$) rate correspond to the simulated compressive ($\varepsilon_{11} < 0$) and tensile ($\varepsilon_{11} > 0$) planar biaxial strains along x- and y-axis respectively, whereas $\varepsilon_{33}(\%)$, presents the induced out-of-plane deformation rate due to the relative displacement along the z-axis. ($a_0 = b_0$) are the optimized equilibrium lattice constants, while ($a = b$) represent the new lattice parameters induced from the strained structure of Si_{46} .

The Formulas (2) and (3) are often used to model the lattice mismatch between an epitaxial grown thin film on a given substrate, which imposes its lattice parameters on the epitaxial film, consequently induces internal strain. For the obtained stable structure in-plane lattice parameters a and b are calculated and fixed at the values corresponding to a desired strain

Table 1

Optimized lattice parameters and atomic positions of type-I guest-free silicon clathrate Si_{46} (space group $Pm\bar{3}n$ (223)) using the GGA-PBE approximation.

Lattice parameter $a_0(\text{\AA})$															
10.22 ^a		10.406 ^b		10.19 ^c		10.069 ^d		10.229 ^e		10.055 ^f		10.20 ^g		10.069 ^h	
Atom		Site: Wyckoff notation		X		Y		Z							
Si(1)		6c (x, y, z)		0.25 ^{a,b,c,f}		0 ^{a,b,c,f}		0.5 ^{a,b,c,f}							
Si(2)		16i (x, x, x)		0.1836 ^a		0.1836 ^a		0.1836 ^a							
				0.1839 ^b		0.1839 ^b		0.1839 ^b							
				0.1835 ^c		0.1835 ^c		0.1835 ^c							
				0.1840 ^d		0.1840 ^d		0.1840 ^d							
Si(3)		24k (0, y, z)		0 ^{a,b,c,d}		0.3079 ^a		0.1170 ^a							
						0.3070 ^b		0.1176 ^b							
						0.3077 ^c		0.1174 ^c							
						0.3080 ^d		0.1170 ^d							

^a This work (GGA-PBE).

^b Data from Ref. [43] (HF-LCCO: Hartree-Fock linear combination of crystalline orbitals).

^c Data from Ref. [44] (LDA: Local density approximation).

^d Data from Ref. [45] (LAPW: Linearized augmented Plane Wave-LDA).

^e Data from Ref. [46] (GGA-PBE).

^f Data from Ref. [42] (TBTEMD: Tight binding total energy molecular dynamics).

^g Data from Ref. [47] (GTBMD: Generalized tight-binding molecular dynamics).

^h Data from Ref. [52] (LDA).

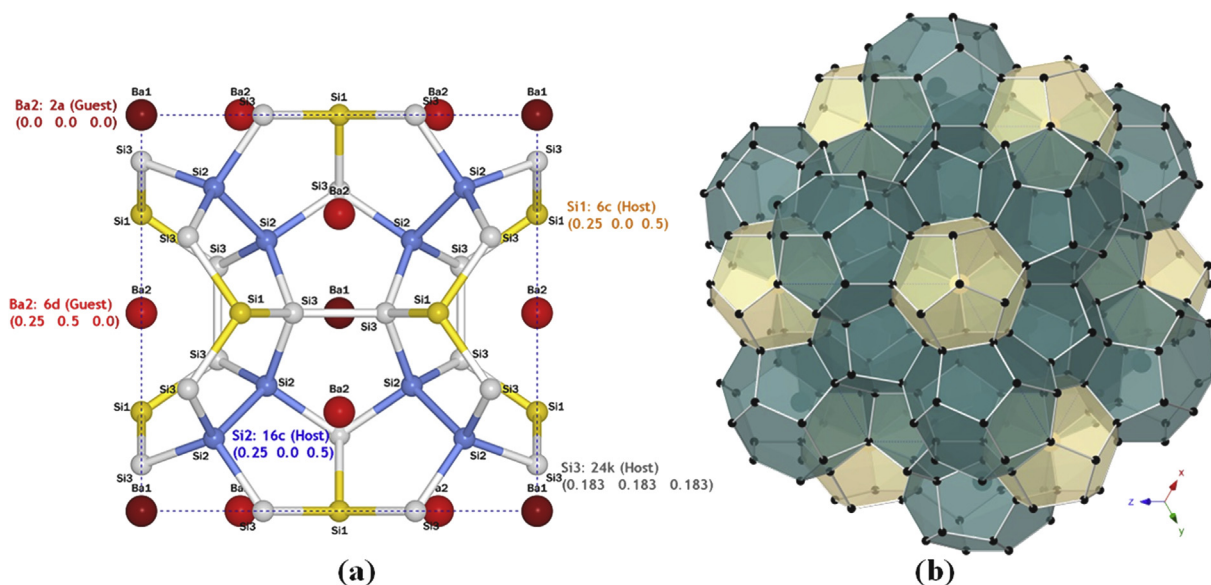


Fig. 1. Aspect of the crystalline structure of type-I Silicon clathrate X_8Si_{46} , (space group: $Pm\bar{3}n$, No 223). (a) A unit cell of $\text{Ba}_8\text{Si}_{46}$ containing 46 Si atoms occupying the following positions according to the Wyckoff notation: Si1(6c) (yellow), Si2(16i) (gray), Si3(24k) (blue), (6d and 2a) (dark and light red) are occupied by eight Ba guest atoms. (b) Two types of polyhedrons (Si_{20} (yellow) + Si_{24} (green)) forming the type-I X_8Si_{46} clathrate framework with guest atoms inside (view down the (111) direction). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

rate, while the out-of-plane lattice parameter c is relaxed along with the internal atomic coordinates of the strained lattice using the BFGS optimization algorithm [33–36], keeping same criterions as described in the computational procedures section. Calculations including strain between -4% (compressive) to $+4\%$ (tensile) by steps of 1% were considered.

3. Results and discussion

3.1. Electronic properties of unstrained Si_{46}

Fig. 2 depicts the calculated band structure with (a) GGA-PBE and (b) GGA-BLYP. In both figures the path of k -vector in the first Brillouin zone is chosen to follow the X-R-M- Γ -R high symmetry segments, and the Fermi energy is set to the zero energy reference. According to the chosen Ultrasoft pseudopotentials in GGA-PBE, each silicon atom is modeled using the following electronic configuration $\text{Si}:[\text{Ne}] 3s^2 3p^2$ as given in Ref. [29], where 92 valence bands were considered. We have chosen 20 empty bands for setting the conduction bands in both cases. For the unstrained state, Si_{46} exhibits an indirect bandgap with semiconductor feature, where the valence band maximum (VBM) appears between M(1/2,1/2,0) and $\Gamma(0,0,0)$ segment, whereas, the conduction band minimum (CBM) lies at the X(1/2,0,0) point. The band structure of Si_{46} was investigated from theoretical point of view. So far, no experimental data is reported due to the difficulty of obtaining a guest free type-I Si_{46} cages where silicon stabilize under diamond structure during synthesis. For the present calculated band structure, comparison with guest-containing clathrates (such as $\text{Na}_8\text{Si}_{46}$) is possible since all type-I clathrates obey the rigid-band model, which means that all those compounds will have similar allures of band structures and differ only in the Fermi level position and the bandgap magnitude, which is affected by the type of the guest atom [45]. In this work we report a quasi-direct band gap equal to $E_g = 1.364\text{eV}$ (GGA-PBE) and $E_g = 1.618\text{eV}$ (GGA-BLYP). It is well-known that the ground state DFT calculations have a tendency to underestimate the bandgap [56], however, our results are in fair agreement with previous theoretical data: $E_g = 1.26\text{eV}$ [40], 0.9eV [45], and 1.315eV [57]. As illustrated in Fig. 2(a) and (b), band structures of unstrained Si_{46} indicate that the valence band is subdivided to two major regions counting each 46 band: the lower valence band (LVB) between -11eV and -4eV , which is mainly formed by a large electronic contribution of the $3s$ - and small contribution of $3p$ -states of Si atoms. Whereas, the upper valence band (UVB between -3eV and 0eV) is formed by a large contribution from $3p$ -states and a very small contribution from $3s$ -states. The conduction band (CB) is dominated by the $3p$ -states of silicon atoms. Total and partial density of states DOS plot illustrated in Fig. 3, were also computed using regular GGA-PBE and hybrid GGA-BLYP functionals. Fig. 3(a) (GGA-PBE) indicates that the Si–Si bonding within the system is covalent and comes from the contribution of $3p^2$ and $3s^2$ states forming strong (sp^3) hybridization, in agreement with the common electronic features of silicon based structures. Thus, Fig. 3(b) (GGA-BLYP) shows similar allure of total DOS and an extra electronic contribution from Si-d orbitals.

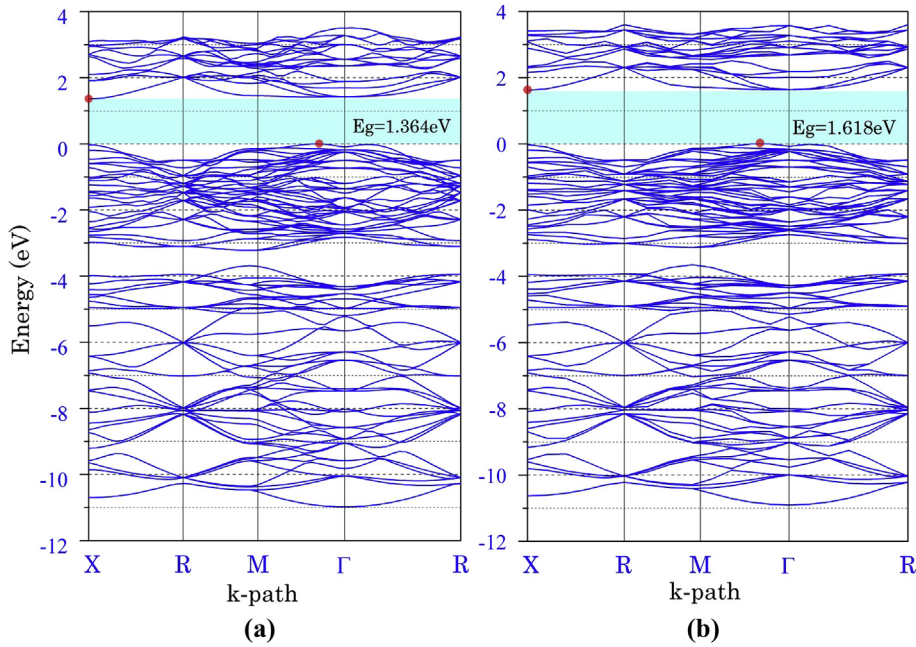


Fig. 2. The calculated band structure of unstrained type-I silicon clathrate Si_{46} using (a) GGA-PBE and (b) hybrid GGA-BLYP functionals with Castep and Dmol³ respectively. Valence band maximums VBM and Conduction band minimums CBM are indicated in red dots. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. Electronic properties under biaxial strain

In order to investigate the effect of the applied planar biaxial-strain on the electronic properties of Si_{46} clathrate, electronic band structures were computed for each step of tensile and compressive biaxial strains ranging from -4% to $+4\%$. The calculated bandgap magnitude versus biaxial-strain is illustrated in Fig. 4. Under biaxial strain, magnitude of bandgap changes significantly where a maximum value of 1.395 eV is reached at tensile strain of $+1\%$, it starts to decrease for higher tensile strains, while, for compressive strains below 0%, it decreases significantly until reaching its minimum value of 0.935 eV at -4% . Fig. 5 depicts the electronic band structures for -1% (a), -2% (b), -3% (c), -4% (d) $+1\%$ (e), $+2\%$ (f), $+3\%$ (g) and $+4\%$ (h) strained Si_{46} . We notice from these figures that the bandgap nature remains quasi-direct for compressive strains. For $\Delta a/a_0 = -3\%$ and -4% the valence band maximum is located in the $\Gamma(0,0,0)$ - $R(0,1/2,1/2)$ high symmetry segment, and the conduction band minimum remains at the X point. For the unstrained and the $\Delta a/a_0 = -1\%$, -2% , $+1\%$ and $+2\%$ states, the VBM will transit to the segment between $\Gamma(0,0,0)$ and $M(1/2,1/2,0)$ the bandgap remains indirect though and the CBM still at the X point. For tensile strains equal and superior to $+3\%$ the valence band maximum VBM shifts down from its previous position between Γ and R, and appears at the X($1/2,0,0$) point to coincide with the CBM leading to the transformation of the quasi-direct bandgap into a direct bandgap. For more insight Fig. 6 exhibits the influence of the biaxial strain on the higher valence bands of the unstrained and $+3\%$ – -3% strained Si_{46} . Fig. 7 shows the variation of the total density of states as a function of the applied strain, it indicates the increasing of the magnitude with the decreasing of the strain condition.

3.3. Optical properties under biaxial strain

All optical properties of materials are quantified by means of the frequency-dependent complex dielectric function $\epsilon(\omega)$, expressed as: $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, which represents the linear response of the system to an external electromagnetic excitation [58]. The imaginary part $\epsilon_2(\omega)$, is computed from the momentum matrix elements taking all possible transitions between the occupied and unoccupied wave functions following the selection rules [59,60] using the following formula:

$$\epsilon_2(\omega) = \left(\frac{2e^2 \pi^2}{m^2 \omega^2} \right) \sum_{ij} \int \langle i|M|j \rangle^2 f_i(1-f_j) \delta(E_f - E_i - \omega) d^3k \quad (4)$$

where: i and j are the initial and final states, M represents the dipole matrix, f_i is the Fermi distribution function for the i th state and E_i is the energy of the electron in this state.

The real part $\epsilon_1(\omega)$ is extracted from the imaginary part through the following Kramers-Kronig formulation [59,60]:

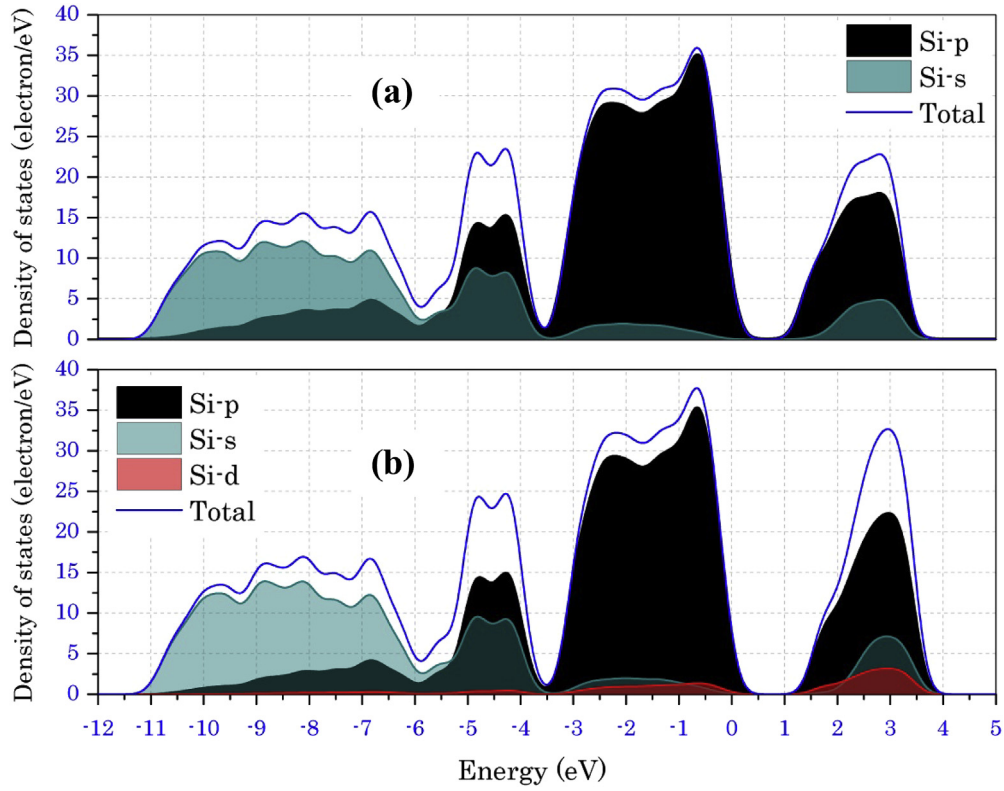


Fig. 3. The calculated total and partial density of states for unstrained type-I silicon clathrate Si_{46} using (a) GGA-PBE and (b) hybrid GGA-BLYP functionals with Castep and Dmol³ respectively.

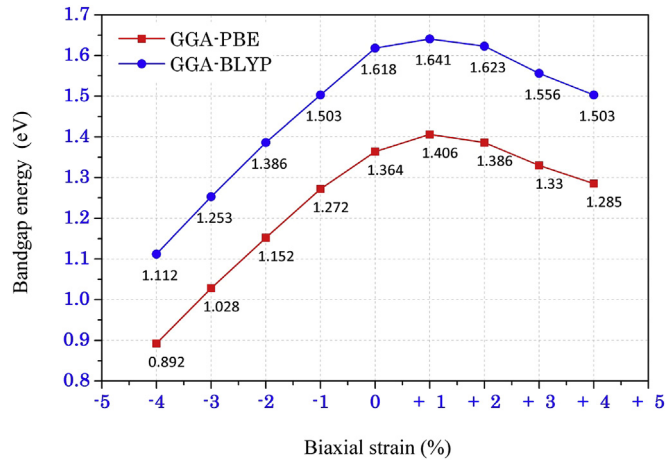


Fig. 4. Band gap magnitude as a function of biaxial strain for type-I Si_{46} calculated using GGA-PBE and hybrid GGA-BLYP.

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^{\infty} \frac{\omega' \varepsilon_2(\omega') d\omega'}{(\omega'^2 - \omega^2)} \quad (5)$$

From the complex dielectric function, other important optical properties such as absorption coefficient $\alpha(\omega)$ can be extracted. In this context, we have computed using GGA-PBE the complex dielectric function and the absorption coefficient as a function of the incident light energy for each rate of biaxial strain. Fig. 8 shows the calculated imaginary and real parts of the

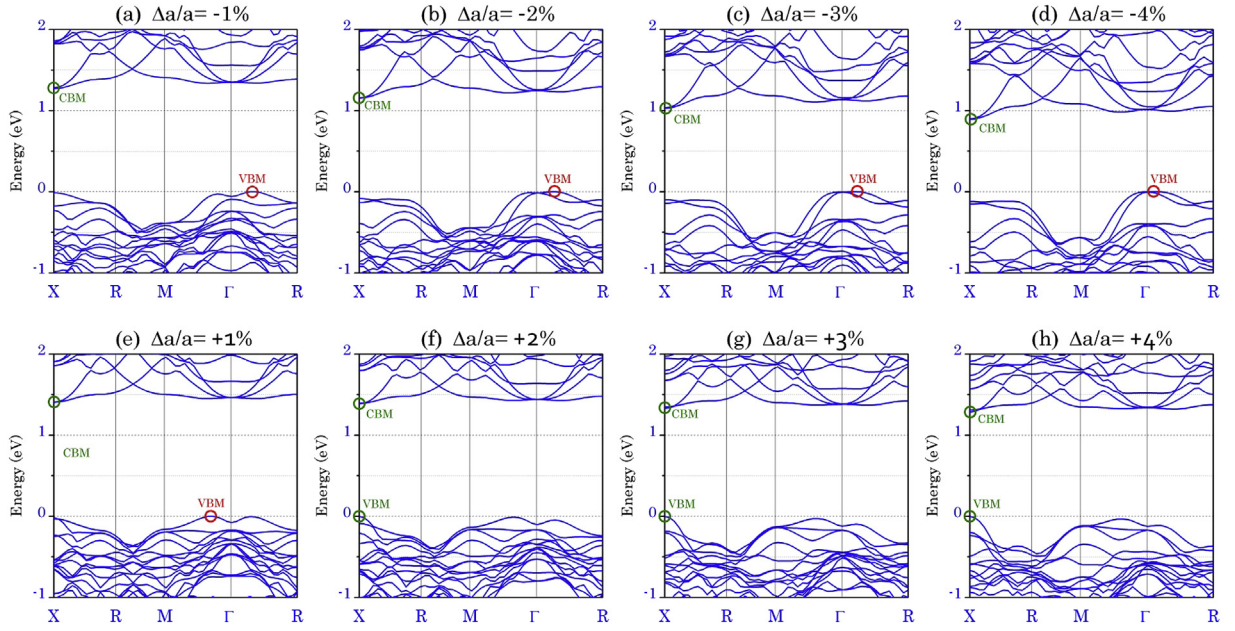


Fig. 5. Electronic structures of strained Si_{46} : (a) -1% , (b) -2% , (c) -3% , (d) -4% , (e) $+1\%$, (f) $+2\%$, (g) $+3\%$ and (h) $+4\%$. VBM and CBM points are indicated in colored circles. For strains ($>+2\%$) the bandgap is direct @ $X(1/2,0,0)$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

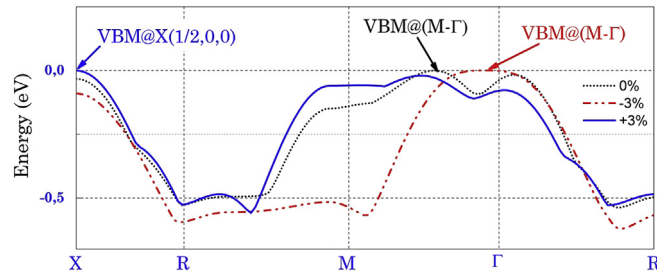


Fig. 6. Valence band maximum VBM of Si_{46} as function of biaxial strain.

complex dielectric function for strained and unstrained Si_{46} following two different polarizations, i.e. the (001) transversal polarization (parallel to c-axis) and (100) normal polarization (perpendicular to c-axis). The real part of the dielectric function is calculated and illustrated in Fig. 8(a) and (b) following the (001) and (100) polarizations respectively. Results in Fig. 8(a) are clearly enhanced for the -4% compressively-strained Si_{46} , the maximum peak is located at 2.5eV and the minimum is found at 4.5eV energy. Fig. 8(b) shows better values for the $+4\%$ tensile-strained Si_{46} , and the extreme peaks appear at the same values of energies as precedent, hence, the three plots have similar shapes, and tend towards zero for higher energies. Fig. 8(c) displays the imaginary part of the dielectric function calculated through the (001) plan. The -4% compressively-strained Si_{46} shows the highest magnitude curve and the maximum peak appears at about 3.8eV energy, while the minimum magnitude is obtained for the $+4\%$ strained Si_{46} at 3.2eV , the unstrained Si_{46} shows a maximum peak at 3.5eV energy. For the imaginary part calculated through a polarization following the (100) plan illustrated in Fig. 8(d), it can be noticed that the $+4\%$ strained Si_{46} reveals highest magnitude, while the lowest is obtained for the -4% strained state, this improvement is related to the direct nature of the band gap obtained for tensile strains above $+3\%$.

Absorption coefficient is among the most relevant quantities to evaluate if the material of interest appears to be promising for optoelectronics, photonics or photovoltaic applications; it is directly derived from the dielectric complex function through the Formula (6) [59]:

$$\alpha(\omega) = \frac{2k\omega}{ch} \quad (6)$$

Where: ω and c represent the incident light frequency and the celerity of the light in vacuum respectively. Fig. 9 shows the computed absorption coefficient for -4% , $+4\%$ and unstrained Si_{46} as a function of energy following the (001) polarization

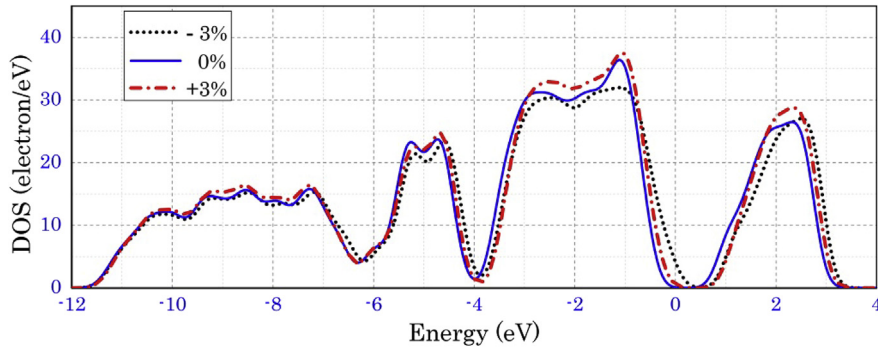


Fig. 7. Influence of biaxial strain on the total density of states of type-I Si_{46} .

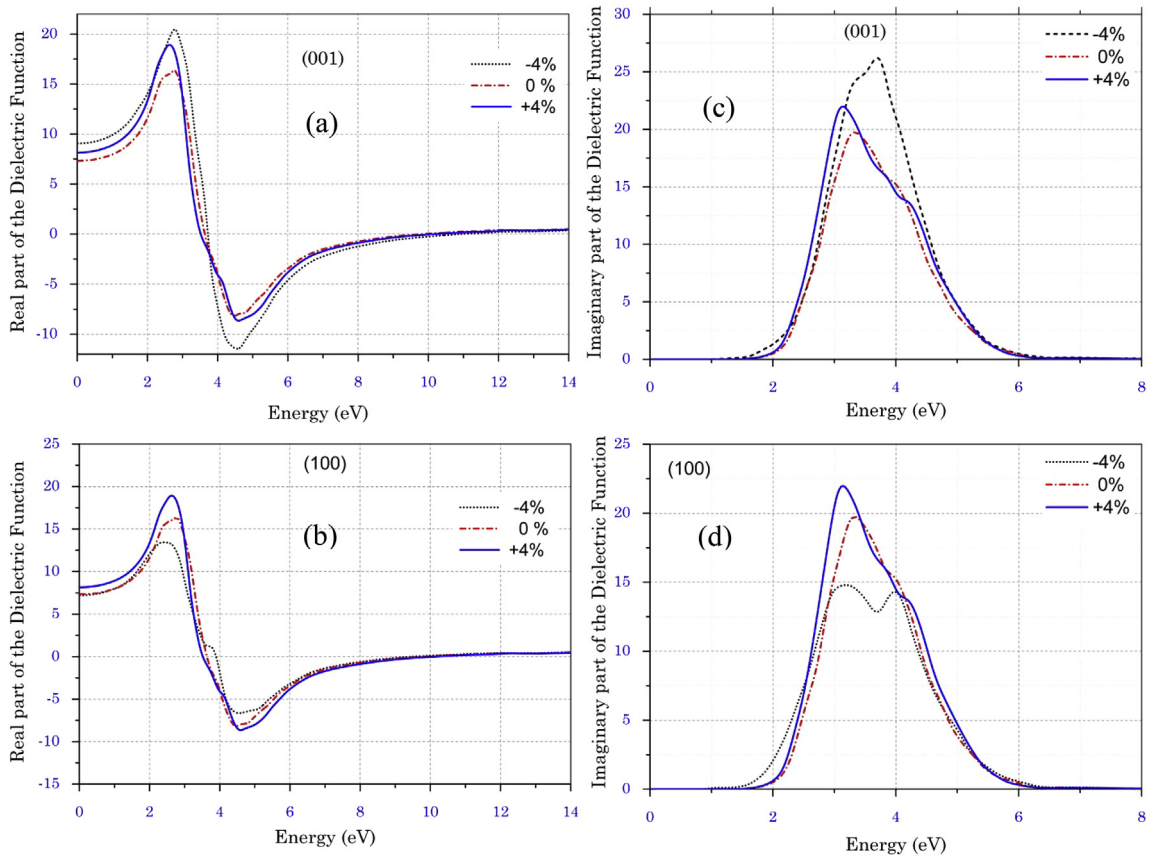


Fig. 8. GGA-PBE calculated dielectric function for type-I guest-free Si_{46} , the real part following (a) the (001), and (b) the (100) plans, the imaginary part following (c) the (001) and (d) the (100) crystallographic plans.

plan, it is noticed that for the tensile biaxial strain of +4% in which the bandgap is direct, the absorption is higher than that of the unstrained or compressively-strained Si_{46} . For unstrained Si_{46} , the maximum peak appears at 4.81 eV energy, the magnitude of the peaks decrease for the -4% state, while, for the +4% state, the major peak appears at 4.94 eV and the general magnitude of absorption spectrum is increased by 17.5%. This improvement is directly attributed to the direct bandgap at +4%. The magnitude is at the order of 2.7×10^4 in the visible range within the electromagnetic spectrum (1eV–4eV). It is primordial to report that in spite of optical transitions are expected to be forbidden in this class of materials according to [44,61], turning the bandgap into direct through biaxial-strain approach might be a solution to overcome this shortage, therefore, this hypothesis needs to be confirmed through further investigations.

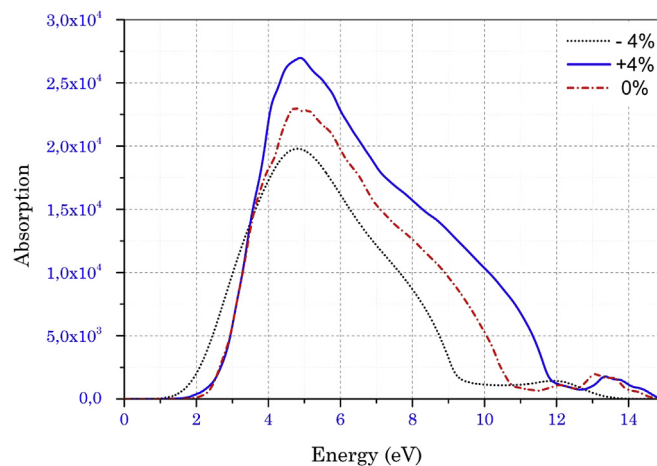


Fig. 9. Optical absorption as a function of energy of unstrained and strained Si₄₆ along the (001) c-axis perpendicular plane.

4. Conclusion

In summary, we have investigated by means of first-principles calculations the effect of planar biaxial-strain on electronic and optical properties of the type-I guest-free silicon clathrate Si₄₆. It was demonstrated that this material could exhibit a direct bandgap under tensile-strains above +2% with magnitudes of 1.381 eV (GGA-PBE) or 1.623 eV (GGA-BLYP). At this rate, optical properties are clearly enhanced with increasing values for the dielectric function as well as the optical absorption. The tensile biaxial strain of +2% corresponds to a substrate lattice constant of about $a = 10.40$ Å, an adequate substrate to exert this strain can be searched following a systematic study. This finding indicates that the material in question is advantageous for direct bandgap applications such as optoelectronic or photovoltaic devices. We wish this work would provide more perspectives of strain tunability of properties of clathrates regarding their use many technological applications.

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Prediction of optically-active transitions in type-VIII guest-free silicon clathrate Si₄₆: A comparative study of its physical properties with type-I counterpart through first-principles

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(Received 12 August 2017; accepted 6 November 2017; published online 28 November 2017)

We have systematically studied the structural, electronic, and optical properties of two types of guest-free Si₄₆ silicon clathrates using first-principles density-functional theory calculations. The properties are compared between two different crystal structures with the same chemical formula of Si₄₆, type-I, and type-VIII. We apply a hybrid functional approach with the Becke, Lee-Yang-Parr (BLYP) functional and compare the electronic properties with those by generalized gradient approximation (GGA-PBE). The band structures of both clathrates calculated within the GGA indicate semiconducting (insulating) properties with indirect bandgaps of 1.38 and 1.36 eV for type-I and type-VIII, respectively. These band gaps increase to 1.60 and 1.62 eV by using the BLYP hybrid functional. The calculated optical absorption of type-I clathrate is slightly larger than that of type-VIII. Lastly, we also performed a symmetry analysis of optical transitions for both Si₄₆ clathrates. It is found that optical transitions are dipole-allowed at the band-edge located along the Γ -H line for Si₄₆-VIII, while the transitions for type-I Si₄₆ are forbidden by symmetry. It is hoped that this finding will motivate further investigations of optical capabilities of the silicon based type-VIII clathrates for photovoltaic and photonic devices. *Published by AIP Publishing.* <https://doi.org/10.1063/1.4999985>

I. INTRODUCTION

Photovoltaic and thermoelectric technologies can directly convert light and heat into electricity. Both technologies are of interest as major players in the energy market as the global demand for clean and renewable energy is increasing. Therefore, the need for ideal abundant, non-toxic, reusable, and robust materials is the motivating factor behind the intensive theoretical and experimental research. Silicon is a scaffolding element of most of the modern high-tech appliances, owing to its abundance, versatility, recyclability, the stability of its oxide SiO₂, and its mature science and industry. Exploration and exploitation of silicon structures beyond the common diamond phase (d-Si) with desired properties that are compatible with the actual silicon-based industries would be a step closer towards cheap and efficient photonic and thermoelectric devices.

Clathrates based on silicon were first synthesized in 1965.^{1,2} They have attracted great attention in the past three decades for their intriguing physical and chemical properties. Silicon clathrates are inclusion compounds wherein silicon as a “host” material forms a covalently *sp*³ bonded cage-like

framework entrapping “guest” atoms or molecules with weak van der Waals host–guest interactions.³ Silicon clathrates are promising candidates for many technological applications such as semiconductors, superconducting,^{4,5} optoelectronics,⁶ thermoelectrics,^{7,8} photovoltaics,^{9,10} and even regarded as a candidate of electrodes in lithium ion batteries.¹¹ Among them, silicon clathrates named type-I and type-II were the most intensively investigated with more than 120 compounds.^{12,13}

Recently, type-VIII with the same formula as type-I (X₈Si₄₆, X = guest atom) has emerged as a promising candidate for thermoelectrics showing higher figure-of-merit *ZT*, owing to their low thermal conductivity.¹⁴ It has also shown a large number of electron pockets near the band edges.¹⁵ Quaternary type-VIII silicon clathrates of Sr₈Al_xGa_{16-x}Si₃₀ were successfully synthesized. Among them, Sr₈Al₆Ga₁₀Si₃₀ has the maximum power factor of 11 $\mu\text{W cm}^{-1} \text{K}^{-2}$ at 1000 K.¹⁶ Type-VIII clathrates based on tin were also successfully synthesized in single crystals form from Ga and Sn fluxes with both p- and n-type doping.¹⁷ Incorporating copper as a dopant in Ba₈Ga₁₆Sn₃₀ demonstrates the highest values of the figure-of-merit *ZT* among all type-VIII clathrates, where *ZT* values of 0.88 and 1.45 at around 500 K, for the p- and n-type crystals were reported, respectively.¹⁸ Raman spectroscopy measurements showed that the “guest” vibrational frequencies of type-VIII Si clathrates are higher than

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those of type-I. It shows strong guest–host interactions in the clathrates, and it was confirmed that they are best adapted for thermoelectric applications.¹⁹

In this study, we report the electronic and optical properties of type-VIII guest-free Si₄₆ clathrates using first-principles density-functional theory (DFT) calculations. The structural features on the electronic and optical properties are compared with those of type-I clathrates Si₄₆ within generalized gradient approximation (GGA). Guest-free silicon clathrates of type-I and type-VIII are hypothetical structures with promising properties that deserve deeper inspection. Comparison of previous theoretical^{20–23} and experimental works^{16,19,21} shows that both compounds have attractive physical properties with some advantages in the favor of type-VIII clathrate. We also apply hybrid functional approach with Becke, Lee–Yang–Parr (BLYP) functional to compare the electronic properties with those by GGA.

The present paper is organized as follows: Sec. II outlines the theoretical approach including our computational details and the structural aspects of the two clathrates. Section III is dedicated to the discussions of the electronic properties and the differences related to the two structural configurations (clathrate types I and VIII). The optical properties are discussed in detail in Sec. IV. Finally, in Sec. III C, we discuss the optical transitions in both allotropes by means of symmetry-analysis based on group theory.

II. THEORETICAL APPROACH

A. Computational procedures

In the present work, the electronic and optical properties were studied using first-principles calculations based on the density functional theory (DFT)^{24,25} as implemented in CASTEP (Cambridge Serial Total Energy Package)²⁶ and Dmol³ (Ref. 27) codes. In the CASTEP code, the Kohn and Sham equations in the DFT framework are solved with ultrasoft pseudopotentials proposed by Vanderbilt.²⁸ The generalized gradient approximation (GGA) proposed by Perdew–Burke–Erzenhorf (PBE) was used in the exchange and correlation energy (XC).²⁹ For silicon based materials, the physical properties calculated by GGA are fairly in agreement with experimental values. The values of ionization energy and optimized crystallographic parameters are closer than those by the local density approximations (LDA).^{30,31} For both types of Si₄₆ clathrates, the self-consistent-field (SCF) calculations were carried out under the criterion for the convergence of the total energy of 5×10^{-4} eV/atom and 0.001 GPa for pressure. The plane-wave kinetic cutoff-energy, E_{cut} , was set to be 480 eV. The first Brillouin zone is sampled into k-grids of $6 \times 6 \times 6$ using the Monkhorst-Pack scheme.³² Before calculating the electronic properties, equilibrium states of the atomic positions at the minimum total energy were obtained using the Broyden–Fletcher–Goldfarb–Shanno optimization algorithm (BFGS).^{33–36} The convergence criteria were set to be 10^{-6} eV/Å, 0.0001 GPa, and 0.05 Å, for the Hellmann–Feynman forces, pressure, and maximum displacement, respectively. For the optical properties, a dense sampling of $18 \times 18 \times 18$ of the first Brillouin zone was used where the total number of irreducible k-points is 165.

Hybrid functional of BLYP^{37,38} was implemented in Dmol3 code. We compare the band structure and density of states (DOS) with those by GGA-PBE. Dmol3 is a powerful DFT code that can include dispersion-correction (DFT-D) for van der Waals interaction into BLYP hybrid functional. This has been proven to produce excellent results for silicon clusters in comparison with LDA.³¹ The range of global orbital cut-off scheme was set to be 4.6 Å, and dispersion-correction proposed by Tkatchenko and Scheffler³⁹ was used. A polarization *d*-function is added to each silicon atom through the use of a double numerical plus polarization basis set (DNP).⁴⁰ The calculated lattice parameters were taken from the fully optimized structure calculated by GGA-PBE in CASTEP code, and then self-consistent calculations were performed by using dense k-sampling meshes of $(10 \times 10 \times 10)$ with 75 irreducible k-points. The valence electronic configurations of each Si atom are chosen to be Si:[Ne] 3s² 3p².²⁸ It is important to consider that the effects of polarizations from the *d*-orbitals are added for silicon atoms within the BLYP functionals.³¹ In this case, the electronic configuration of silicon atoms will be set as (Si:1s² 2s² 2p⁶ 3s² 3p² 4s¹ 3d¹), where the *Si-4s* and *Si-3d* orbitals are empty and used as “virtual orbitals” in order to enhance the charge redistribution, which gives a better estimation for the electronic properties. In this work, we have chosen 60 empty bands for setting the conduction bands in both clathrates.

B. Structural details

1. Type-I Si₄₆

Type-I silicon clathrate with a chemical formula of M₈Si₄₆ has a cubic structure with the space group of Pm-3n (#223), where the guest-free Si₄₆ unit includes 46 atoms, which can be formed by a compact arrangement of eight face-sharing cages: two dodecahedrons Si₂₀ (a “platonic” solid with twelve pentagonal faces and 20 atoms, usually referred to as: [5¹²]), plus six tetrakaidecahedron Si₂₄ (12 pentagonal faces and two hexagonal faces with 24 atoms symbolized as: [5¹²6²]).^{3,13,41} The vacant cavities inside the cages are usually filled by “guest” atoms such as alkaline or alkali-earth metal species. In this structure, the “host” silicon atoms occupy three Wyckoff positions: 6c, 16i, and 24k, while the guest atoms occupy the 2a and 6d positions of the space group. In this study, no guest atoms are considered. Figure 1(a) shows a unit cell of type-I X₈Si₄₆ including the Wyckoff positions. Figure 1(c) illustrates the two initial polyhedrons forming the Si₄₆ main lattice. To determine the equilibrium lattice constants of type-I Si₄₆ theoretically, we carried out lattice optimizations. The optimized lattice parameter within GGA-PBE is $a = 10.23$ Å. As listed in Table I, our obtained results are compared with those calculated by different first-principles methods. As no experimental data for guest-free type-I Si₄₆ are available at the present, we employed experimental structures of Ba₈Si₄₆ and Ba₈Cu₄Si₄₂ for comparison.^{12,42} ($a = 10.33$ and 10.32 Å, respectively). The volume difference between our optimized Si₄₆ and the experimental Ba₈Si₄₆ structures is attributed to the size of the barium guests.⁴³

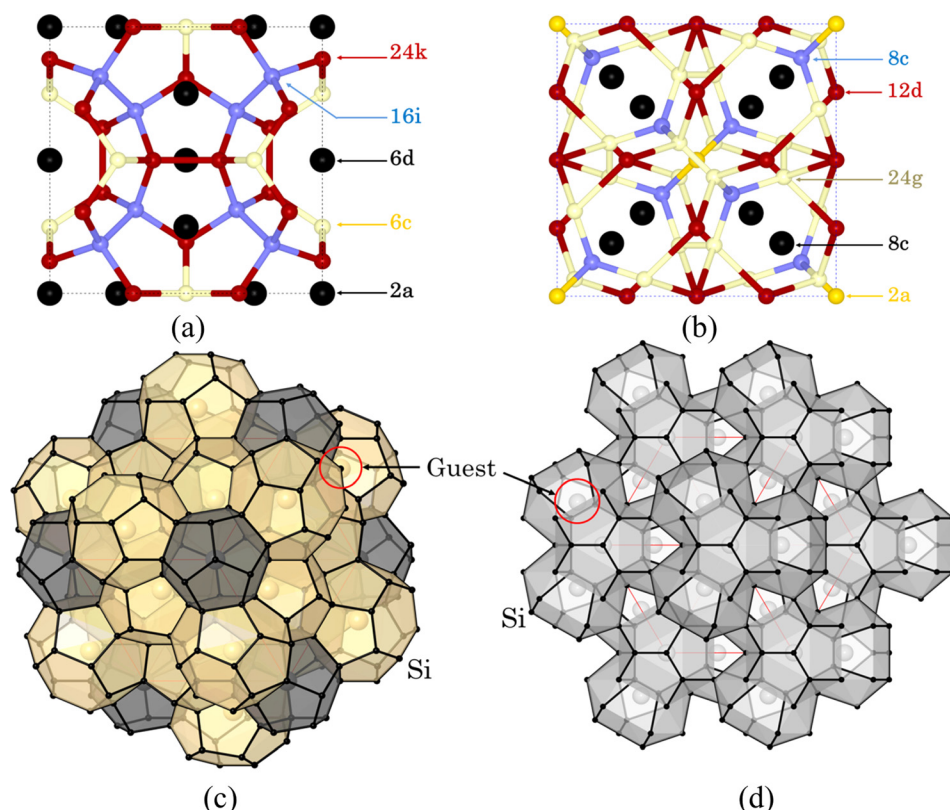


FIG. 1. Crystal structures of type-I (a) and type-VIII (b) guest containing silicon clathrates X_8Si_{46} , with Wyckoff atomic positions (the dark gray balls are guest atoms X). Polyhedral representation of type-I (c) and type-VIII (d) guest-free Si_{46} down the (111) direction.

2. Type-VIII Si_{46}

Type-VIII silicon clathrate with the same chemical formula as for type-I phase (allotropic forms of the same clathrate compound) crystallizes in the body-centered cubic with the space group of $I4-3m$ (#217). The main framework of type-VIII clathrate is formed by the combination of only one type of strongly distorted dodecahedral cages (S_{23}), the host atoms of silicon occupy four Wyckoff positions: 2a, 12d, 24g, and 8c, whereas the guest atoms M occupy the 8c sites. Figure 1(b) shows the configuration of a unit cell of type-VIII M_8Si_{46} silicon clathrate. The dodecahedral cages forming the main unit cell of type-VIII Si_{46} are illustrated in Fig. 1(d). The equilibrium lattice parameters of type-VIII Si_{46} (VIII- Si_{46}) was obtained within GGA-PBE by using the same BFGS procedure with the same parameter sets as for clathrate type-I. The optimized lattice constant is $a = 10.10 \text{ \AA}$, which is smaller than type-I. Our values are in a fair agreement with the literature shown in Table I. Table II lists the structural parameters of the type-I and type-VIII Si_{46} obtained after optimization of the structures. The optimized bond length range was 2.35–2.42 $\text{\AA}$. Similar to the I- Si_{46} clathrate, no experimental data are available for either the guest-free or binary type-VIII X_8Si_{46} silicon clathrate. Since only framework-substituted type-VIII was successfully synthesized, we employed experimental lattice parameters of the ternary silicon clathrate single crystal of $Sr_8Al_xGa_{16-x}Si_{30}$ ($a = 10.44 \text{ \AA}$) reported by Shimizu *et al.*¹⁹

III. RESULTS AND DISCUSSION

A. Electronic properties

Calculated band structures and densities of states (DOS) for type-I and type-VIII Si_{46} using GGA-PBE are plotted in

Fig. 2, and band structure with BLYP hybrid functional are shown in Fig. 3. The bandgaps for type-I and type-VIII- Si_{46} within GGA-PBE (BLYP) are 1.38 eV (1.62 eV) and 1.36 eV (1.61 eV), respectively. The band gaps calculated with BLYP are generally larger than that with GGA-PBE. Both materials exhibit semiconducting (insulating) behaviors with indirect band gaps in the optimum visible range of the electromagnetic spectrum. Our results are in fairly good agreement with previously reported data (Table I). The conduction band minimum CBM and the valence band maximum VBM of type-I clathrate are both located at a k -point along the Γ -X line [Fig. 2(c)], in agreement with Ref. 43. On the other hand, in type-VIII Si_{46} , the VBM is located at N-point ($1/2, 0, 0$) and the CBM appears along the Γ -H line [Fig. 2(d)], and our result agrees with a previous report.¹⁵ In the valence band (VB) of type-I Si_{46} , the energy bands from Γ to R point are degenerated, and the valence band valleys at X, M, R, and Γ are lower in energy than the VBM by 0.06, 0.20, 0.53, and 0.13 eV, respectively. For type-VIII, the VB valleys for the H, P, and Γ points are located below the VBM by 0.21, 0.04, and 0.39 eV, respectively.

For type-I Si_{46} , the VB can be subdivided into two major regions separated by a small energy gap estimated at 0.47 eV by GGA-PBE. As shown in Fig. 4(a), In the partial density of states (PDOS) calculated by GGA-PBE, the lower valence band (LVB: from -11 eV to -4 eV) is composed from large contributions of 3s and small amount from 3p orbitals, whereas the upper valence band (UVB) from -3 eV to 0 eV has large contributions from the 3p-states and very small contribution from the 3s-states of silicon atoms. In contrast, the VB of type-VIII Si_{46} is continuous. As shown in the Fig. 4(b) (upper part), the majority of the contributions are from

TABLE I. Lattice parameters, bond-length, mass densities, bandgaps, and positions of valence band maximum (VBM) and conduction-band minimum (CBM) for guest-free silicon clathrate Si_{46} in type-I and -VIII phases as calculated by GGA-PBE and BLYP in comparison with the literature.

Space group	Type-I Si_{46} Pm3-n (No223)	Type-VIII Si_{46} I4-3m (No 217)
Lattice parameter a (Å)	10.233 ^a 10.229 ^b 10.355 ^c 10.19 ^d 10.229 ^c 10.317 ^e 10.40 ^j	10.1002 ^a 10.10 ^b 10.1015 ^c 10.10 ^f
Si-Si distance range (Å)	(2.357–2.402) ^a (2.380–2.430) ^c	(2.353–2.417) ^a
Density ρ (g cm ⁻³)	2.01 ^a 2.004 ^b	2.12 ^a 2.082 ^f
Bandgap energy E_g (eV)	1.38 ^a (1.620) ^a 1.314 ^b 2.5 ^c 1.26 ^d 0.9 ^h 1.315 ⁱ 1.31 (1.95) ^k	1.36 ^a (1.62) ^a 1.24 ^b 1.24 ^f
Nature of bandgap	Indirect	Indirect
VBM@	Γ -X ^{a, d, h, i}	N (1/2, 0, 0) ^{a, b}
CBM@	Γ -X ^{a, d, h, i}	Γ -H ^{a, b}

^aOur results by GGA-PBE and (GGA-BLYP).

^bData from Ref. 15 GGA-PBE.

^cData from Ref. 44 Tight binding-like Molecular Dynamics TBMD.

^dData from Ref. 43 LDA.

^eData from Ref. 20 GGA-PBE.

^fData from Ref. 45 GGA-PBE.

^gData from Ref. 46 Molecular Dynamics MD-Lennard-Jones (LJ) Potentials.

^hData from Ref. 47 LDA-LAPW.

ⁱData from Ref. 48 GGA.

^jData from Ref. 49 Hartree-Fock HF.

^kData from Ref. 50 GGA-PBE and (HSE).

3p-states, while contributions from 3s-states are noticed to increase when going toward lower energies. The conduction bands for both type-I and type-VIII Si_{46} are dominated by large contributions from 3p-states and smaller contributions from the 3s-states as depicted in Fig. 4. Differences in the electronic properties of the two clathrates are directly related to the nature of their polyhedral cages, the way they combine,

TABLE II. Atomic positions (Wyckoff notation) of type-I and type-VIII guest-free clathrates (Si_{46}) as optimized by GGA-PBE in comparison with the literature.

Si_{46} -I	Si_{46} -VIII
$6c$ (x, y, z)	(0.25, 0, 0.5) ^{a,b,c,d}
$16i$ ($x=y=z$)	(0.1836) ^a (0.684) ^b (0.186) ^c (0.1837) ^d
$24k$ (x, y, z)	(0, 0.308, 0.1170) ^a (0, 0.883, 0.692) ^b (0, 0.307, 0.1176) ^c (0, 0.1172, 0.3077) ^d
	$2a$ ($x=y=z$)
	(0) ^{a,b,c}
	$8c$ ($x=y=z$)
	(0.36455) ^a (0.384) ^b
	$12d$ (x, y, z)
	(0.25, 0.5, 0) ^{a,b}
	$24g$ ($x=y, z$)
	(0.415, 0.143) ^{a,b}

^aOur results (GGA-PBE).

^bData from Ref. 20 GGA-PBE.

^cData from Ref. 49 Hartree-Fock (HF).

^dData from Ref. 44 Tight binding-like Molecular Dynamics TBMD.

and the nature of their respective polygonal faces. In type-I Si_{46} , two types of cages combine to form the main lattice (dodecahedron Si_{20} + tetrakaidecahedron Si_{24}). The Si_{20} contains twelve pentagonal rings [5¹²] and the Si_{24} cage contains twelve pentagonal rings plus two hexagonal faces [5¹²6²]. In this case, the dodecahedrons are not related to each other but are connected to other Si_{24} cages through the pentagonal faces only, while the Si_{24} cages are connected to each other by sharing their two six-fold hexagonal faces. They form a sort of long columns along the three crystallographic directions, as described by Dolyniuk *et al.*¹³ Type-VIII lattice is formed by the association of only one type of strongly distorted dodecahedral cages Si_{23} , which, additionally to the five- and six-fold rings, possess three non-flat seven-fold rings (Si_{23} is described as: [5³6³7³]). In type-VIII structure, the cages are connected mainly through sharing their pentagonal faces; as each cage has three of them, it will connect with three other cages thoroughly, while it will connect to other cages through non-flat six- and seven-fold faces. This imperfect yet solid inter-cage connection leads to the formation of inter-cage cavities (vacant 8-vertex polyhedral cages). The main structural differences discussed herein are directly correlated with major differences in the physical and chemical properties.

The main differences in band structures between type-I Si_{46} clathrate and the Si_2 diamond structure are due to the fact that there are only six-fold polygonal rings in the Si_2 lattice, while in type-I Si_{46} clathrate lattice, 87% are six-fold and 13% are five-fold rings.⁴³ Thus, for the Si_2 lattice, the valence band is continuous and larger due to the significant overlap of the 3s- and 3p-states (−12 eV to 0 eV), whereas, for type-I Si_{46} , the presence of the five-fold rings prevents the s-orbitals from forming complete anti-bonding states. The highest 3s-like state is therefore lower in energy than that of the Si_2 , and becomes lower than the lowest 3p-like state, leading to an opening of a gap between 3s- and 3p-like states. An extensive analysis of the electronic signature of the pentagonal rings in silicon clathrate was carried out by Mélinon *et al.*⁵¹ By combining experimental and theoretical work, they demonstrate that the introduction of pentagonal rings into the diamond lattice induces a merging of the s- and sp-like bands, which reduce the valence band width. Similar analysis can be inferred from our results. In type-VIII Si_{46} , lattice contains only one type of strongly distorted dodecahedron Si_{23} , which is derived by breaking three edges and adding three new vertices to the regular pentagonal dodecahedra Si_{20} .¹³ Such a dodecahedral cage is equally composed by one-third of five-folds, one-third of non-flat six-folds, and one-third of non-flat seven-fold rings (see Fig. 5). The presence of seven-fold rings will allow the s-states to overlap again with the 3-p states to make the valence band continuous yet larger than that of type-I counterpart. Therefore, the bandgap of type-VIII Si_{46} is slightly smaller than type-I bandgap as also predicted by Norouzzadeh *et al.*¹⁵

B. Linear optical properties

The indirect nature of the band gaps of both silicon clathrates materials is considered as a limiting factor regarding their use for photonics or photovoltaics. Inducing an

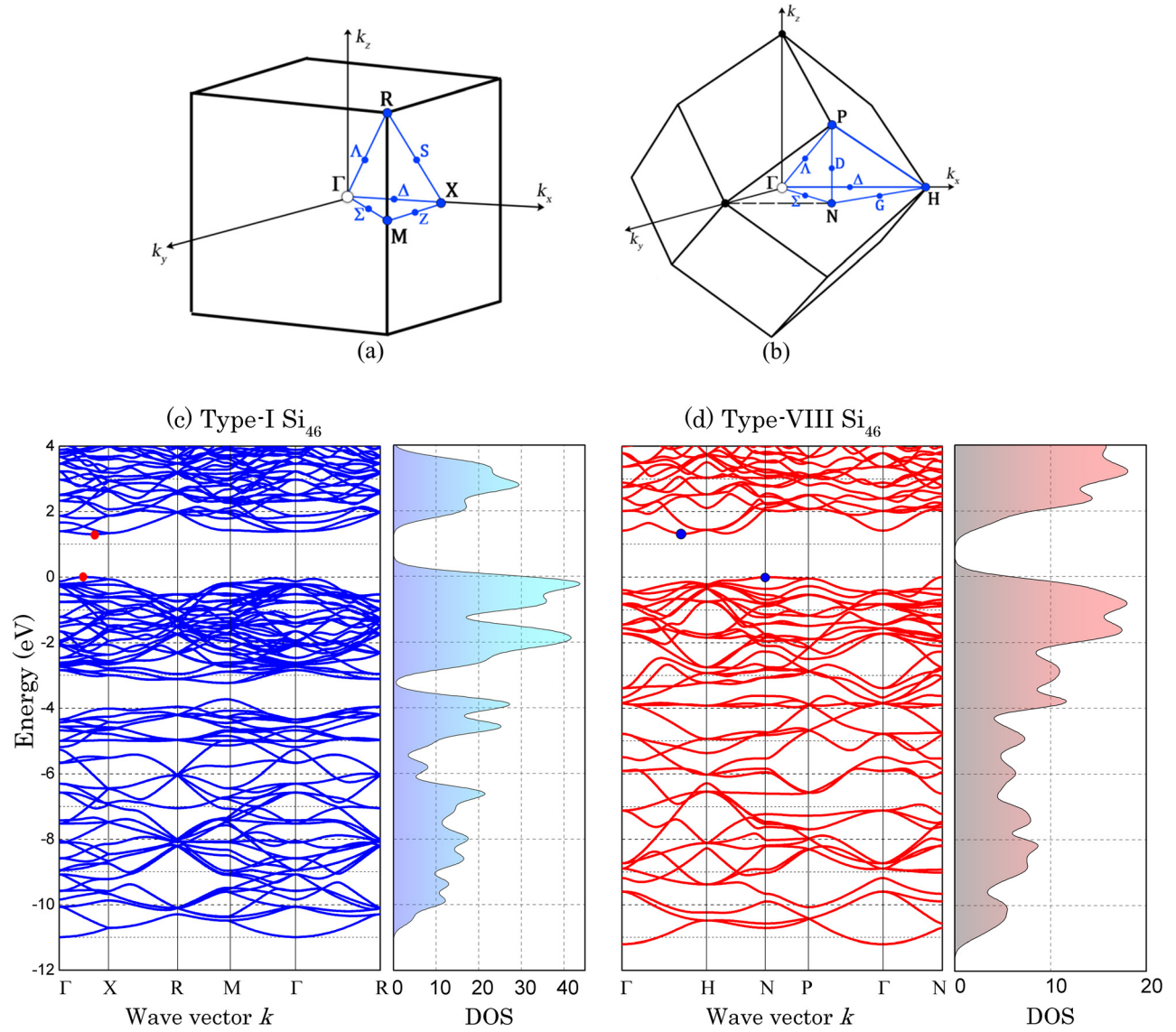


FIG. 2. First Brillouin zones of (a) type-I (Pm3-n) and (b) type-VIII (I4-3m) cubic clathrates obtained through their reciprocal lattices. Band structures and total density of states (DOS) of (c) type-I Si₄₆ within GGA-PBE, the band structure is calculated along the symmetric line of $\Gamma(0,0,0)$ -X(1/2,0,0)-R(1/2,1/2,1/2)-M(1/2,1/2,0)- Γ -R. (d) Band structure and total density of states (DOS) for type-VIII Si₄₆ within GGA-PBE along the symmetric line of $\Gamma(0,0,0)$ -H(1/2,1/2,-1/2)-N(1/2,0,0)-P(1/4,1/4,1/4)- Γ -N.

indirect-direct bandgap transition in type I clathrate was already predicted through the effect of biaxial tensile strain.⁵² This prediction could be experimentally verified if an appropriate substrate was chosen for the growth of silicon

clathrates in thin film form, which could open a plethora of applications for an all-silicon material in optoelectronics. However, there are only few studies on the optical properties for type-I so far, and actually still no data are available on

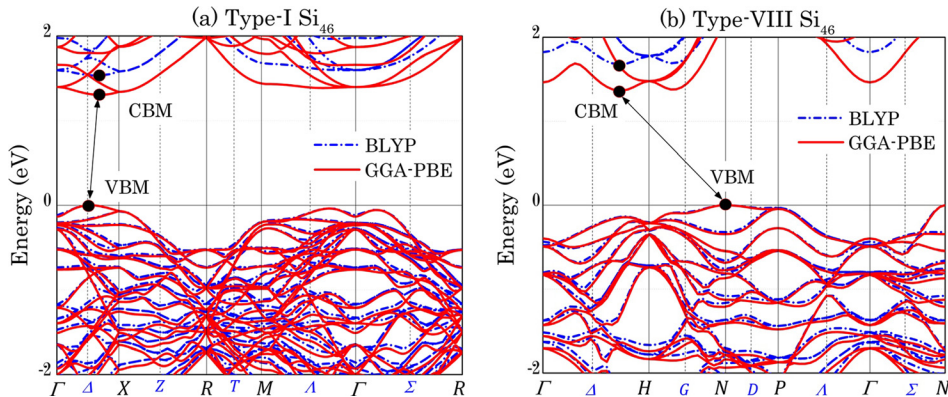


FIG. 3. (a) and (b) represent the comparison between GGA-PBE (CASTEP) and BLYP (Dmol³) band structures along the Γ -X-R-M- Γ -R and Γ -H-N-P- Γ -N k -paths for type-I and type-VIII Si₄₆ clathrates, respectively. The Fermi energy is set to be the zero energy reference.

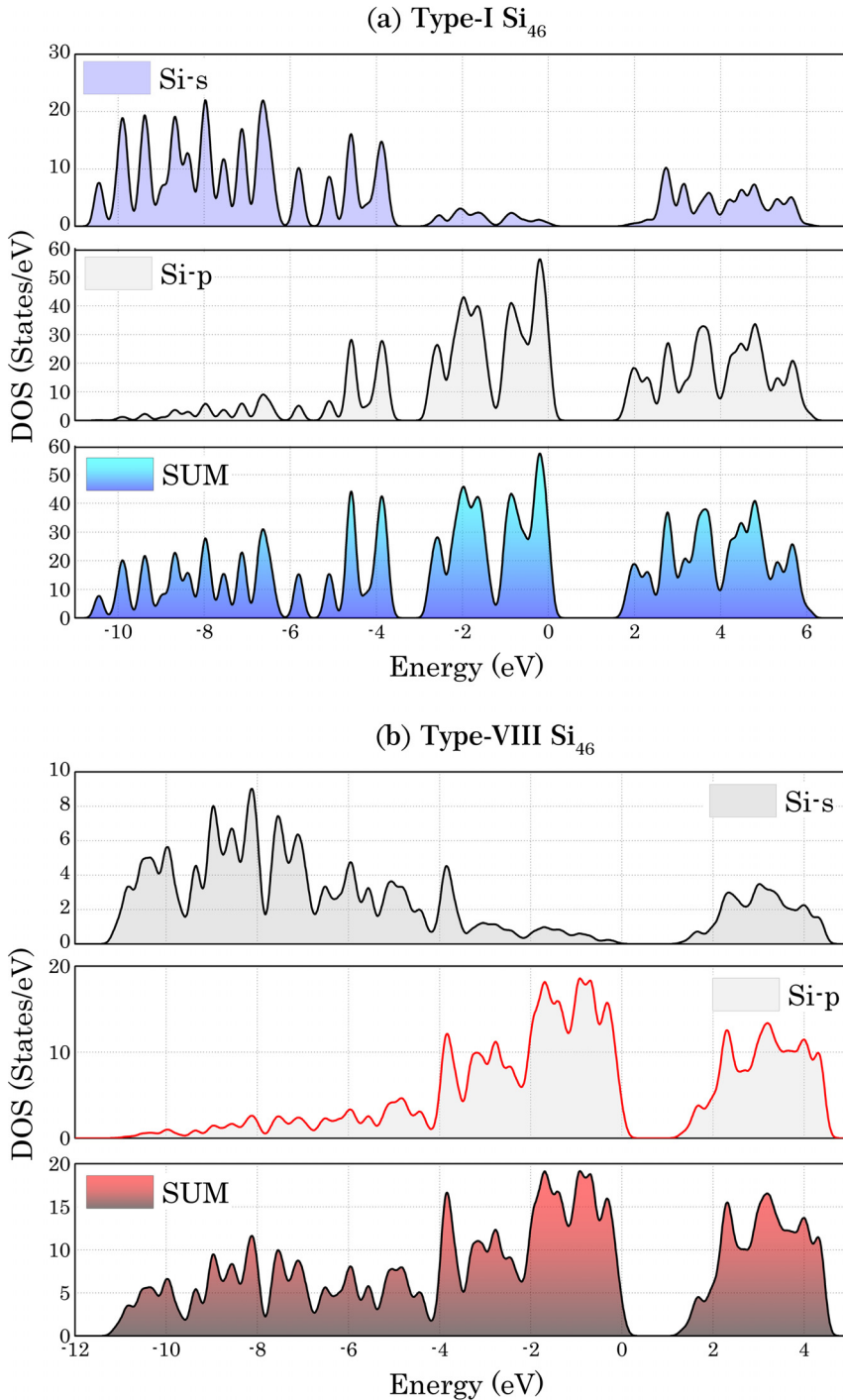


FIG. 4. Partial and total densities of states (DOS) for (a) type-I and (b) type-VIII guest-free silicon clathrates Si₄₆ calculated by GGA-PBE using CASTEP package.

type-VIII Si₄₆ clathrate. In the present part of the work, we attempt to clarify some fundamental optical properties for both clathrates in their equilibrium states at ambient pressure.

Optical properties of materials are expressed through the frequency-dependent dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. It represents the linear response of the material to an external electromagnetic field. It is strongly related to the photon–electron interaction within the matter.⁵³ The imaginary part, $\varepsilon_2(\omega)$, is computed from the matrix elements that take all possible transitions between the occupied and unoccupied wave functions within the Fermi's golden selection rules, which can be written by using the following formula:^{54,55}

$$\varepsilon_2(\omega) = \left(\frac{4e^2\pi^2}{m^2\omega^2} \right) \sum_{ij} \int \langle \psi_i | M_{if} | \psi_j \rangle^2 f_i(1-f_j) \delta(E_f - E_i - \omega) d^3k, \quad (1)$$

where ψ_i and ψ_j represent the initial and final states, respectively, M_{if} is the dipole operator, f_i is the Fermi distribution function for the i th state and E_i is the energy level of the valence electron in this eigenstate. The real part $\varepsilon_1(\omega)$ is extracted from the imaginary part through the Kramers-Kronig formulation^{54,55}

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega') d\omega'}{(\omega'^2 - \omega^2)}. \quad (2)$$

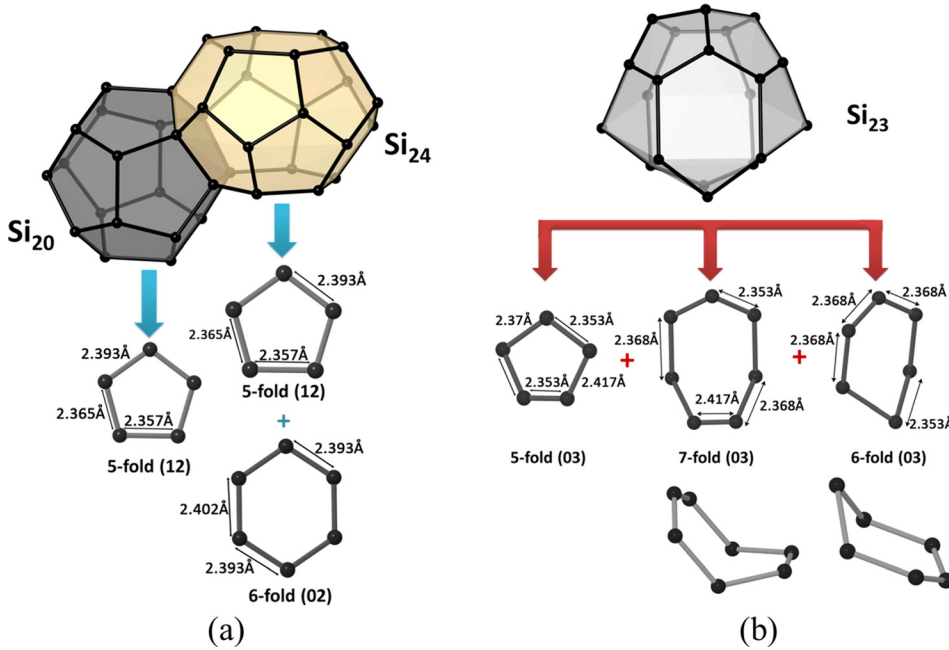


FIG. 5. Elemental polyhedral cages and their respective polygonal faces and their numbers (between parentheses) in each cage for: (a) type-I and (b) type-VIII Si_{46} . The seven- and six-fold rings in type-VIII material are not flat due to the strong distortion of the dodecahedrons Si_{23} .

In this study, we have computed the dielectric functions as well as the absorption coefficients for the theoretically optimized structures of both guest-free Si_{46} clathrates. Figures 6(a) and 6(b) display the imaginary and real parts of the calculated dielectric function, respectively. In both clathrates, the imaginary part of the dielectric function $\epsilon_2(\omega)$ is located in the energy range of 0 to 8 eV. The absorption edge of type-VIII is positioned at lower energy than that for type-I. The difference of threshold energies corresponds to band gap values of 1.377 eV and 1.360 eV, approximately.

The $\epsilon_2(\omega)$ curves exhibit sharp spectrums where the maximum peaks are located at 3.27 eV (3.34 eV), and the second peaks are located at 3.97 eV (3.59 eV) for type-I (type-VIII) Si_{46} . In order to determine the origins of the peaks, here, we consider only the direct interband transitions and neglect the indirect phonon-assisted transitions. For both clathrates, due to the strong sp^3 bonding of the silicon networks, the main peaks of $\epsilon_2(\omega)$ are all generated from the electronic transitions from the top of the valence band to the bottom of the conduction bands along the corresponding valleys in the high-symmetry k-vector path. For type-I Si_{46} , the first peak originates from the $\text{Si-}2p$ (−0.5 eV) to $\text{Si-}3s$ (1.87 eV) interband transitions at the R point; however, it has

been reported that the optical interband transitions in type-I Si_{46} are shown to be dipole-forbidden along Γ , Γ -X(Δ), and X-M(Z) high symmetry points.⁵⁶ Whereas located at 2.46 eV for type-VIII Si_{46} , the first small peak may originate from the $\text{Si-}3p$ (−0.45 eV) to $\text{Si-}p$ (1.85 eV) transition at the Λ low-symmetry point. The real part of the dielectric function $\epsilon_1(\omega)$ is plotted in the Fig. 6(b) and shows similar behavior for both materials with slightly higher values for type-VIII Si_{46} . Major peaks appear at 2.71 eV and 3.06 eV and the minimum peaks are at 4.97 eV and 5.23 eV for type-I and type-VIII, respectively. The zero frequency limit of the real part $\epsilon_1(0)$, which represents the electronic part of the static dielectric constant that strongly depends on the bandgap magnitude and nature, is estimated in our case as 11.24 and 12.3 for type-I and type-VIII Si_{46} , respectively. Additionally, $\epsilon_1(\omega)$ becomes negative within the ranges of 4.07 to 13 eV (4.20 to 13 eV) for type-I (type-VIII) Si_{46} , and both figures tend toward zero for higher energies.

Several recent studies has proven that group-IV clathrates can provide high absorption coefficients^{9,57–59} compared with their diamond phase counterpart. Silicon clathrates can be promising candidates used for optical, optoelectronic, and photovoltaic applications. Figure 7 illustrates the optical

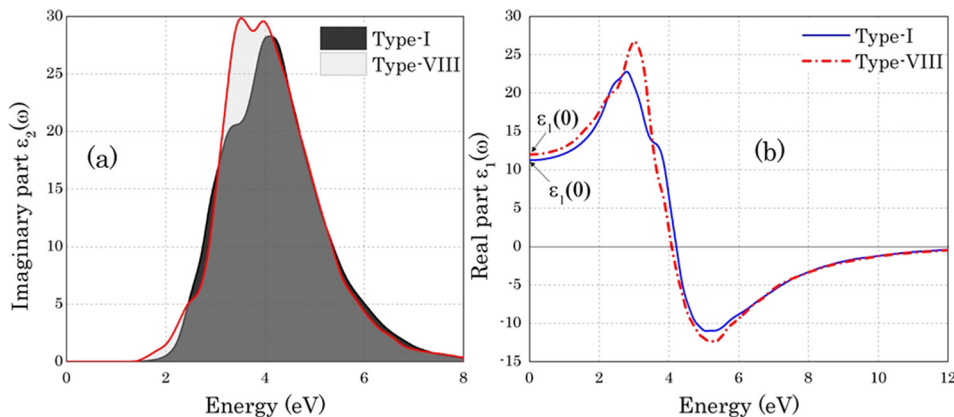


FIG. 6. (a) Imaginary and (b) real parts of the complex dielectric function calculated by GGA-PBE as a function of the energy for type-I and type-VIII Si_{46} clathrates.

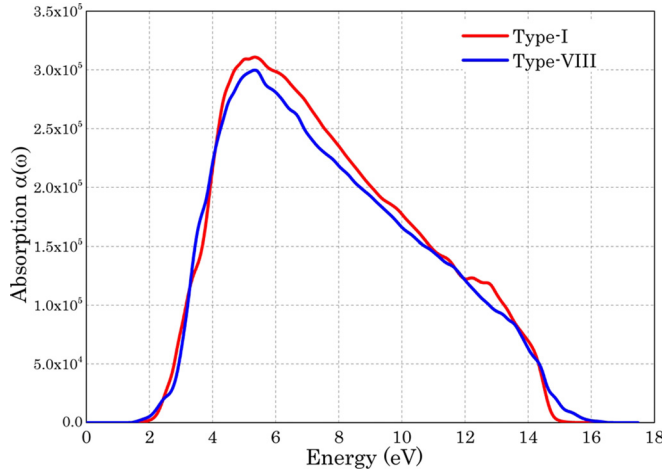


FIG. 7. Optical absorption as a function of energy calculated by GGA-PBE for type-I and type-VIII Si_{46} clathrates.

absorption as a function of the incident light energy for type-I and -VIII Si_{46} in the range of 0–18 eV. The fundamental absorption edges are located at 1.24 eV and 1.20 eV, whereas the maximum peaks are positioned at 5.26 and 5.27 eV for type-I and type-VIII Si_{46} , respectively. After reaching their maximum values, absorption coefficients for both materials start decreasing rapidly toward zero, which is a characteristic for semiconducting behavior. We have computed the absorption coefficients for type-I and type-VIII Si_{46} by means of GGA-PBE using $18 \times 18 \times 18$ dense sampling of the first Brillouin zone giving 165 k-points for each system. The absorption coefficient represents a measure of the rate of decay in the light intensity that crosses the material. It is usually expressed as a fraction of absorbed light energy per distance unit (cm^{-1}). It is directly derived from the complex dielectric function through the formula (12) given by

$$\alpha(\omega) = \frac{2k\omega}{ch}, \quad (3)$$

where: ω and c are the incident light frequency and the speed of the light in vacuum, respectively.

For type-VIII, the absorption spectrum is slightly lower in magnitude than its type-I counterpart. Our calculations of the absorption coefficient and the dielectric function demonstrate a great potential for optical applications for both type-I and type-VIII structures. This may invite further experimental and theoretical research for possible applications in photovoltaic or photonic devices.

C. Symmetry analysis and optical transitions

In this section, we study the dipole-allowability of the optical transitions by means of symmetry-analysis using our GGA-PBE results. Firstly, we have to consider our materials as pure periodic crystals as the symmetry-analysis is held within the bulk form. Symmetry-analysis study is primordial in order to have a deep insight into the possible direct optical transitions that can be (if dipole-allowed by symmetry) a factor in favor of using the investigated materials for photovoltaic and photonic devices. Furthermore, symmetry analysis

allows us to evaluate the interband transitions and the symmetry of the important energy bands and their respective point groups at high and low symmetry points in the Brillouin zone. Connétable⁵⁶ has extensively investigated, the optical transitions for intercalated and empty type-I X_8Si_{46} and type-II X_6Si_{34} silicon clathrates ($\text{X} = \text{Xe}, \text{I}, \text{Te}, \text{Sn}$) using symmetry-analysis from LDA results.⁵⁶ It has been demonstrated that most of the interband transitions are dipole-forbidden at the band edges in type-I and type-II clathrates except for the type-II Xenon-doped $\text{Xe}_6\text{Si}_{34}$ clathrate at the low symmetry point $\Lambda(\text{C}_{3v})$, where the transition was found to be dipole-allowed. However, analysis of the optical transitions for type-VIII Si_{46} has not been reported so far. In the following, we present a study of the interband optical transitions in both clathrates types using the group theory approach. As discussed previously, the VBM and CBM for type-I are both located within the Γ -X line, whereas, they are respectively located at N and Γ -H line for type-VIII Si_{46} . The symmetries of the first three valence bands and the two first conduction bands, at several high- and low-symmetry points in the first Brillouin zone are taken into consideration for both clathrates. The wave-vector path along the high symmetry points of ($\Gamma, \text{X}, \text{M}, \text{R}, \text{H}, \text{N}, \text{P}$) were chosen by using the compatibility relations tables available in the literature for the simple cubic SC (type-I, $\text{Pm}\bar{3}\text{-n}$, no223) and the body centered cubic BCC (type-VIII, $\text{I}\bar{4}\text{-3m}$, no217) systems.^{60,61} We adopt the Schoenflies notations to designate the point groups and their irreducible representations (IRs).⁶² The high and the low symmetry points in the first Brillouin zone of both materials are illustrated in Fig. 2.

In type-I Si_{46} , the Γ belongs to the O_h point group, whereas, Δ and Z k-points belong to the C_{4v} and C_{2v} point groups, respectively. For type-VIII Si_{46} , the Γ belongs to the T_d point group, while the points H, N, and P have the T_d , the C_{2v} and the T_d symmetries, respectively. The point groups of the low symmetry points for VIII- Si_{46} i.e., the Δ , G, D, Λ , Σ are C_{2v} , C_s , C_{2v} , C_{3v} , and C_s symmetries, respectively. The irreducible representations (IRs) for each point group are taken from the character of wavefunctions at each k-point. For the VIII- Si_{46} at the $\Gamma(\text{T}_d)$, the first valence band has the A_2 representation, the second and third valence bands are

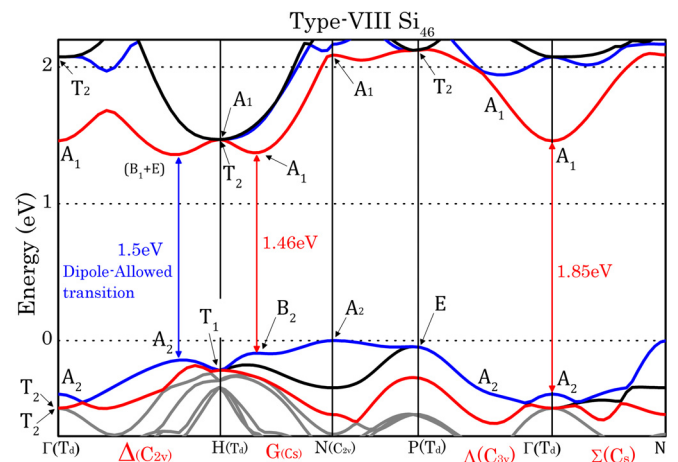


FIG. 8. Symmetry classifications of energy bands for type-VIII Si_{46} clathrate.

TABLE III. Symmetries, point groups and irreducible representations for type-I (O_h) and type-VIII (T_d) Si_{46} silicon clathrates. The energies are calculated from the VBM along each symmetry k -point from GGA-PBE band structures. Between brackets are indicated the Irreducible Representation for each energy band. Point groups symbols are given in Schoenflies notation.⁶²

Si ₄₆ -I				Si ₄₆ -VIII				
Γ (O_h)	Δ (C_{4v})	Z (C_{2v})		Γ (T_d)	Δ (C_{2v})	H (T_d)	G (C_s)	N (C_{2v})
Conduction bands								
	E (eV)					E (eV)		
E_{c2}	+2.00 ^a +1.59 ^b [A _{2g}]	+1.66 ^a +1.45 ^b [B ₁]	+1.92 ^a +1.45 ^b [B ₁]	+2.07 ^a [T ₂]	+2.15 ^a [B ₁]	+1.477 ^a [A ₁]	+1.97 ^a [A']	+2.43 ^a [B ₁]
E_{c1}	+1.63 ^a +1.32 ^b [T _{1u}]	+1.55 [A ₁ + E] ^a +1.23[A ₁] ^b	+1.65 ^a [A ₁ + B ₁ + B ₂] ^a 1.30 ^b [A ₁]	+1.46 ^a [A ₁]	+1.55 ^a [A ₁]	+1.477 ^a [T ₂]	+1.72 ^a [A'']	+2.43 ^a [A ₁]
Valence Bands								
E_{v1}	-0.11 ^a -0.13 ^b [A _{1u}]	0.00 [A ₂] ^a 0.00 [A ₂] ^b	-0.14 ^a -0.15 ^b [A ₂]	-0.39 ^a [B ₂]	-0.153 ^a [B ₂]	-0.2164 ^a [T ₁]	-0.095 ^a [A']	0.00 ^a [A ₂]
E_{v2}	-0.11 ^a -0.23 ^b [T _{2g}]	-0.13 [B ₂ + E] ^a -0.19 [B ₂] ^b	-0.18 ^a -0.20 ^b [A ₂]	-0.49 ^a [T ₂]	-0.30 ^a [B ₁]	-0.2164 ^a [E]	-0.23 ^a [A']	-0.347 ^a [A ₁]
E_{v3}	-0.20 ^a -0.24 ^b [E _u]	-0.22 [A ₂ + B ₂] ^a -0.26 [E] ^b	-0.23 [A ₂ + B ₁] ^a -0.33 [B ₂] ^b	-0.49 ^a [T ₁]	-0.31 ^a [A ₁]	-0.2164 ^a [T ₂]	-0.331 ^a [A']	-0.541 ^a [B ₁]
Irreducible representation of the electron momentum operator P								
	[T _{1u}] ^{a,b}	[E + A ₁] ^{a,b}	[A ₁ + B ₁ + B ₂] ^{a,b}	[T ₂] ^a	[A ₁] ^a	[T _{1g}] ^a	[A''] ^a	[A ₂] ^a
Optical transition?								
	No	No	No	No	YES	No	No	No

^aOur data (GGA-PBE).

^bData from Ref. 56 (LDA). Optical transitions are checked using selection rules within the group theory.

merged together at Γ and they have the T_2 representation. The upper valence bands are mainly constructed from 3p orbitals and minor contributions from 3s-states. At this region, the Γ , H, and P k -points of the upper valence bands tend to merge (see Fig. 8). In contrary, at low symmetry k -points, energy bands tend to separate except for Δ and Λ lines. This is due to the hybridization mechanism with anti-symmetric combinations of the s and p-orbitals, which is similar to the hybridization mechanism in type-I Si_{46} and in other Si clusters as well.⁵⁶ The IRs at Γ for the first conduction band in type-VIII Si_{46} is A_1 and the second conduction band has the T_2 symmetry. Table III lists the symmetry classifications of the point groups, the energies and the IRs for each energy band near the Fermi level for both types of clathrates.

In order to investigate if the interband transitions are dipole-allowed or forbidden we apply the selection rules for both type-I and type-VIII allotropes. The probability magnitude of the electric dipole transition per unit of time between an initial $|\psi_i\rangle$ and a final $|\psi_f\rangle$ state is proportional to the dipole matrix elements⁶³

$$M_{if} = \langle \psi_i | P | \psi_f \rangle, \quad (4)$$

where P is the electron momentum operator. Calculating the direct-product of the two irreducible representations involved in the dipole matrix elements using the character tables together with the selection rules, will permit us to determine

those interband transitions which are either allowed ($M_{if} \neq 0$) or forbidden ($M_{if} = 0$). For type-I Si_{46} , group theory analysis at the Γ (O_h), Δ (Γ -X) and Z (X-M), shows that all the interband transitions are dipole-forbidden by symmetry, which is coherent with the results of Connétable.⁵⁶

For type-VIII Si_{46} , the direct products between the irreducible representations of the first valence and conduction bands along the Γ (T_d), Δ (C_{2v}), H (T_d) and G (C_s) k -points are calculated and summarized in Table III. We also include in Table III the irreducible representations of the momentum operator P (T_d), which are necessary for the calculations of the dipole matrix elements of the interband transitions. The three components of the momentum operator p_x , p_y , and p_z

TABLE IV. Characters of the irreducible representations of the T_d point group. The bottom part represents the direct product between the IRs of the first conduction and valence bands along the $\Gamma(0, 0, 0)$ k -point for type-VIII Si_{46} .

IRs	E	8C ₃	3C ₂	6S ₄	6σ _d	Linear, rotations	Quadratic functions
Γ_1	A ₁	+1	+1	+1	+1		$x^2 + y^2 + z^2$
Γ_2	A ₂	+1	+1	+1	-1		
Γ_{12}	E	+2	-1	+2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
Γ_{25}	T ₁	+3	0	-1	+1	(R _x , R _y , R _z)	
Γ_{15}	T ₂	+3	0	-1	+1	(x, y, z)	(xy, xz, yz)
Direct product							
$\Gamma_2 \otimes P(T_2) \otimes \Gamma_1$	+3	0	-1	+1	-1	$A_2 \otimes T_2 \otimes A_1 = A_2$ (Forbidden)	

TABLE V. Characters of the irreducible representations of the C_{2v} point group. The bottom part represents the direct product between the IRs of the first conduction and valence bands along the Γ -H(Δ) k-point for type-VIII Si_{46} .

IRs		E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	Linear, rotations	Quadratic functions	Cubic functions
Δ_1	A_1	+1	+1	+1	+1	z	x^2+y^2, z^2	$z^3, z(x^2+y^2)$
Δ_2	A_2	+1	+1	-1	-1	R_z	...	...
Δ'_1	B_1	+1	-1	+1	-1	...	x^2-y^2	$z(x^2-y^2)$
Δ'_2	B_2	+1	-1	-1	+1	...	xy	xyz
Direct product								
$\Delta_2 \otimes P(A_2) \otimes \Delta_1$		+1	-1	-1	+1	$B_2 \otimes A_1 \otimes A_1 = B_2$ (Dipole-allowed)		

along the Γ -H (C_{2v}) line belong to the irreducible representation T_2 .⁶⁴ As inferred from Tables IV and V, the direct product of the irreducible representations at the $\Gamma(T_d)$ point shows that the electronic transition between the first valence band $E_{v1}(A_2)$ and the first conduction band $E_{c1}(A_1)$ through the momentum operator $P(T_2)$ is equal to (T_1). The direct product at the Γ -H (C_{2v}) between the top valence band $E_{v1}(B_2)$, the momentum operator $P(A_1)$ and the first conduction band $E_{c1}(A_1)$ is equal to (B_2). According to the selection rules, transitions [from an initial state $|\psi_i\rangle$ (E_{v1}) to a final state $|\psi_f\rangle$ (E_{c1})] are dipole-allowed if the direct product of the IRs of the valence band (VB), the momentum operator P , and the conduction band (CB) contain at least one character from the final state's IR.⁶⁴ Therefore, interband transitions the at Γ point are dipole-forbidden, while they are dipole-allowed by symmetry along the Γ -H (Δ) line. This is a very interesting preliminary result that holds promise for type-VIII Si_{46} clathrate as an optoelectronic material. In particular, with its large number of carrier pockets near the band edges,¹⁵ and the possibility to induce an indirect to direct bandgap transition through biaxial strain in thin film form,⁵² we predict very interesting optical and thermoelectric features for Type-VIII silicon clathrates.

IV. CONCLUSIONS

In this study, we have performed first-principles calculations in order to investigate the structural, electronic, and optical properties of type-I and type-VIII guest-free silicon clathrates Si_{46} . We applied a hybrid functional approach with the Becke, Lee-Yang-Parr (BLYP) functional and compare the electronic properties with those by generalized gradient approximation (GGA-PBE). The band structures of both Si_{46} clathrates show semiconducting properties. The band gaps for both type-I and type-VIII calculated with the BLYP hybrid functional are larger than those by GGA-PBE. The main differences in the structural properties of both materials are the source of the differences in their physical and chemical properties. That is specifically, the configuration and the nature of the elemental cages and their constituent polygons. The peak of optical absorption in type-I clathrate is slightly larger than that of type-VIII. However, symmetry analysis has demonstrated that type-VIII Si_{46} has an optically active electronic transition along the Γ -H line that can motivate further theoretical and experimental investigation to assess the possibilities of an all-silicon material for thermoelectric, photovoltaic, and optoelectronic applications.

ACKNOWLEDGMENTS

Author Nassim Ahmed Mahammedi would like to thank the Ministry of Higher Education and Scientific Research - Algeria, for providing scholarship to Japan in the frame of the "Programme National Exceptionnel PNE (Oct 2016 to Oct 2017)". One of the authors, M.F., would like to acknowledge the partial financial support provided by the UWI at Mona under the new initiative grant F:16104P/O:7505/A:760005/P:21.

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A Comparative Study of the Effect of Strain on the Electronic and Optical Properties of Filled and Unfilled $\text{Ba}_8\text{Si}_{46}$ Type I-clathrate

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A first principles calculations study is carried out to theoretically investigate the effect of compressive and tensile strains on the structural, electronic and optical properties of type-I guest-free Si_{46} and barium-filled $\text{Ba}_8\text{Si}_{46}$ clathrates. The electronic band structure of the unfilled Si_{46} clathrate revealed a semiconducting behaviour with a quasi-direct band gap of 1.36 eV. Under hydrostatic pressure, the bandgap magnitude of the guest-free Si_{46} behaves monotonously. For the Ba doped Si_{46} clathrate ($\text{Ba}_8\text{Si}_{46}$) structure, the strain has no significant effect on the electronic band structure, while its impact on the optical properties is appreciable. The optical properties, such as the dielectric function and the absorption were computed for different strain variations, which are clearly enhanced for both the unfilled Si_{46} and Ba-filled $\text{Ba}_8\text{Si}_{46}$ clathrates when the pressure is 1 GPa in the direction of a compressive state.

DOI: [10.12693/APhysPolA.132.836](https://doi.org/10.12693/APhysPolA.132.836)

PACS/topics: First-principles calculations, $\text{Ba}_8\text{Si}_{46}$ clathrates, cage structure mechanical properties, electronic structure properties

1. Introduction

Group-IV inorganic clathrates are cage-like materials where a number of host atoms form a network arranged in cage shape to possibly enclose a guest atom. Indeed, this class of material is very promising given the large possibilities to tune the intrinsic properties by substituting both host and guest atoms in order to design new materials having desired functions for specific applications. Depending on the atomic arrangements eight types of clathrates are well established [1]. The type-I structure is the most investigated among the different known types, on the other hand, it has an excellent thermoelectric [1], semiconducting, and superconducting properties [2]. Guest free type-I Si_{46} silicon clathrate is a hypothetical structure, which has been theoretically studied and expected to exhibit interesting thermoelectric and electronic properties as a promising semiconductor material with a band-gap greater than that of silicon in the diamond structure [3]. However, the actual synthesis of type-I Si_{46} clathrate remains a challenging task and yet not resolved. In contrast with type-I Si_{46} silicon clathrate, the filled $\text{Ba}_8\text{Si}_{46}$ [4] and partially vacant $\text{Ba}_x\text{Si}_{46}$ [5] have been synthesized by different methods, mostly by using techniques based on high pressure and high temperature. The synthesized $\text{Ba}_8\text{Si}_{46}$ material revealed several technological properties, especially it is known as the first clathrate to demonstrate low temperature superconductivity, in addition, by partial substitution of barium with aluminium, $\text{Ba}_8\text{Si}_{46}$ have showed a good semiconducting behaviour [5]. One drawback of

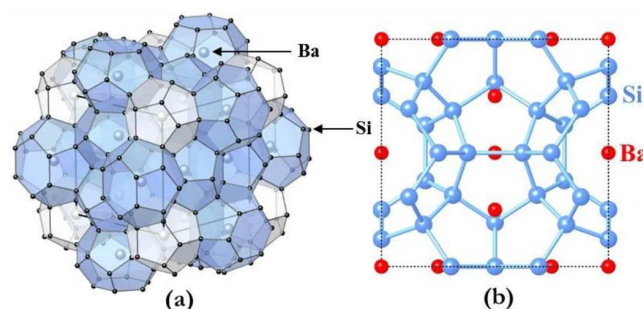


Fig. 1. Atomic configuration of $\text{Ba}_8\text{Si}_{46}$ structure formed by polyhedrons network in (a) and the unit given in (b). Ba and Si atoms are shown respectively in red and in blue color.

this material is related to its low mechanical properties under hydrostatic pressure.

In this work we have systematically investigated the effect of hydrostatic pressure on the electronic and optical properties of $\text{Ba}_8\text{Si}_{46}$ and Si_{46} clathrates in type-I configurations by using first principles calculations in the frame of density functional theory (DFT). The development of the computational techniques for applying DFT to real materials has made it possible to predict quantitatively the atomic and electronic structure and properties of different materials [6–10]. In particular, the pseudopotential method based on the local DFT [7–11] has been very successfully used for studying various properties of the crystals [8], surfaces, and interfaces of metals, ceramics, and semiconductors [12]. The first part deals with

a concise description of the theoretical background; in the second part the structural and electronic aspects of both compounds were examined.

2. Calculation methods

Inorganic clathrates are mainly composed from face-sharing polyhedral networks of group IV atoms (C, Si, Ge, and Sn), entrapping guest atoms like alkaline-earth, rare-earth or alkali-metals, among others. The type-I configuration with formula is X_8A_{46} (X = guest, A = group IV) belongs to the simple cubic in $Pm\bar{3}n$ space group, build-up from association of dodecahedron and tetrakaedricahedron polyhedrons networks as directed in Fig. 1, where host atoms occupy the 2a, 6c, 16i, and 24k symmetric positions, whereas the guest atom species (X) are located in 6d positions according to the Wyckoff designation.

In the present work a first-principles calculation is carried out using Cambridge Serial Total Energy Package (CASTEP) [13] code, based on the DFT [14, 15]. To describe the electric wave function, a plane-wave ultra-soft pseudopotential method is adopted. For the energy minimization the generalized gradient approximation (GGA) is used within the Perdew–Burke–Erzenhorf (PBE) [16] approach. In the present calculation, for accuracy we have set a plane-wave cut-off energy value to 480 eV, and the first irreducible Brillouin zone in the reciprocal space was sampled using $6 \times 6 \times 6$ grid mesh following the Monkhorst–Pack scheme resulting to a total number of 108 k -points. In order to obtain optimal geometrical parameters and internal coordinates, a rigorous atomic relaxation of the system is performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) [17–20] optimization algorithm until obtaining the Hellmann–Feynman atomic forces with a value lower than 10^{-3} eV/Å. Optical properties were computed for each step of the hydrostatic pressure using $14 \times 14 \times 14$ mesh points sampling in the first Brillouin zone for better approximation of the dielectric function.

For the calculated mechanical properties to simulate hydrostatic pressure, an isotropic stress tensor is exerted on the system, the strain response is defined through the Moore law of general elasticity given as follows: $(\sigma_{ij}) = (C_{ij})(\varepsilon_{ij})$, $i, j = 1, 2, 3$, where σ_{ij} are the elements of the tensor matrix, C_{ij} are the elastic constants, and the ε_{ij} represent the elements of the strain tensor. The cubic nature of the type-I lattice leads to define only three elastic constants, i.e. C_{11} , C_{12} and C_{44} which are equal to: $C_{11} = 135$ GPa, $C_{12} = 58$ GPa, and $C_{44} = 40$ GPa as reported in the literature for both Si_{46} and Ba_8Si_{46} clathrates [4]. In the present calculation we have simulated hydrostatic pressure values between -3% to $+3\%$ by a variation step of 1% .

3. Results and discussion

We have calculated the structural properties of both Ba_8Si_{46} and Si_{46} structures considering both applied hydrostatic pressure and without pressure. Knowing the fact

that GGA–PBE calculations underestimate lattice constants and internal coordinates, as shown in Table I, our calculated results exhibit a good agreement with available experimental and other theoretical results. The calculated lattice constants are of $a = 10.0$ Å and $a = 10.22$ Å for the unstrained Ba_8Si_{46} and Si_{46} structures, respectively. Depending on whether compressive or tensile strain is applied, we have found that the lattice parameters vary monotonously with the magnitude of the applied hydrostatic pressure. In our case, the simulated hydrostatic pressure for Be_8Si_{46} do not exceed 15 GPa as reported in [9], which can undergo phase transformation beyond this limit. As for Si_{46} clathrate, the value of 19 GPa is defined as an upper limit referenced to the theoretically predicted in [10]. The calculated structural, electronic, and optical properties for both Ba_8Si_{46} and Si_{46} structure are considered taking into account these limited values of hydrostatic pressures.

TABLE I

Calculated lattice parameter for type-I Ba_8Si_{46} and Si_{46} clathrates structures (GGA–PBE), space group No. 223 ($Pm\bar{3}n$). ^a — this work, (GGA–PBE)

Ba_8Si_{46} -I	Si_{46} -I
10.31^a , 10.328 [11], 10.3177 [12]	10.22^a , 10.20 [10], 10.055 [13]

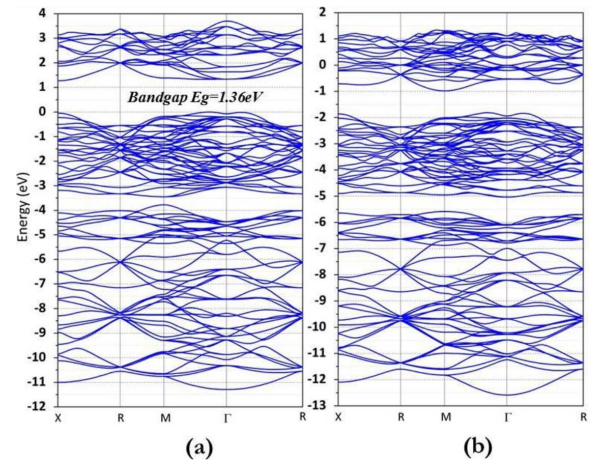


Fig. 2. GGA-PBE calculated energy band structure for the type-I (unfilled) Si_{46} (a) and for the Ba (filled) Ba_8Si_{46} (b).

Figure 2 shows the calculated band structure along X – R – M – G – M high symmetry path of the first irreducible Brillouin zone for the type-I Si_{46} and Ba_8Si_{46} structures under zero hydrostatic pressure. Figure 2a reveals an indirect band gap of 1.36 eV in which the valence band maximum is located between M and G high symmetry points, while the conduction band minimum is located at the X point. The Si_{46} clathrate exhibits a semiconducting character as supported by previous theoretical studies. The transition from semiconducting behaviour to metallic character is observed due to the inclusion of Ba atom as shown in the obtained band structure of Ba_8Si_{46} depicted in Fig. 2b, which results in the mixture, near to the Fermi level, of the $3d$ states of Ba and $2p$ from Si in the Ba–Si bonding. For the case of applied

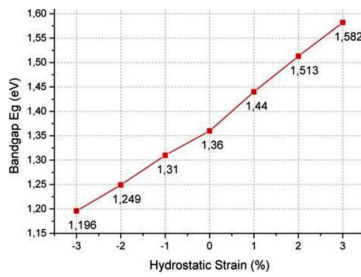


Fig. 3. Variation of the band-gap as a function of hydrostatic pressure for type-I Si_{46} obtained by GGA-PBE approximation.

tensile or compressive hydrostatic pressures, the energy band gap in Si_{46} remains quasidirect, and exhibits minor changes in the energy position of the VBM and CBM, however, the band gap magnitude varies quasi-linearly with the applied strain.

The variation of band gap magnitude as a function of applied pressure is shown in Fig. 3. Under the applied hydrostatic pressure, the band gap magnitude changes monotonously with varying from -3% to $+3\%$ described in Fig. 3. For the case of filled $\text{Ba}_8\text{Si}_{46}$, the applied hydrostatic pressure slightly affects the interatomic distances and cell volumes keeping a monotonous variation with the incremented pressure magnitude. Nevertheless, the effect of the pressure on $\text{Ba}_8\text{Si}_{46}$ modify its optical properties, in particular the complex dielectric function. Figure 4 illustrates the dielectric functions of $\text{Ba}_8\text{Si}_{46}$ as function of the photon energy for $\text{Ba}_8\text{Si}_{46}$ showing respectively the real (Fig. 4a) and imaginary (Fig. 4b) parts of dielectric function for different values of hydrostatic pressure (0, 1, 3, 5, and 7 GPa). It is observed from Fig. 4b that the value ϵ_2 tends to zero more rapidly for the higher pressure in the examined ranges. Figure 4b indicates that the material is susceptible to become transparent at low energy value. It is clear that from Fig. 4 the simulated 1 GPa gives better optical properties as compared to other higher values.

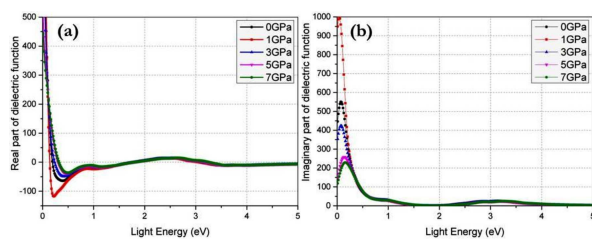


Fig. 4. Calculated GGA-PBE real (a) and imaginary (b) part of the dielectric function as functions of hydrostatic pressure for the type-I filled $\text{Ba}_8\text{Si}_{46}$.

4. Conclusion

In the present study, we have systematically investigated by performing DFT calculations, the structural, electronic and optical properties of the unfilled Si_{46} and filled $\text{Ba}_8\text{Si}_{46}$ type-I clathrates under various pressures. The calculated lattice parameters for both structures Si_{46}

and $\text{Ba}_8\text{Si}_{46}$ are in good agreement with the experimental and former theoretical results. The electronic band structure shows a semiconducting character for Si_{46} structure with a quasi-direct band gap, which turns to a metallic character due to the presence of the Ba atoms. We have found that under the simulated pressure the band gap in Si_{46} remains quasi-direct and its magnitude change noticeably with the pressure variation, while the pressure is less affecting the electronic properties of $\text{Ba}_8\text{Si}_{46}$ but appreciable for its optical properties.

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ملخص:

العنصر الأكثر وفرة على الأرض بعد الأكسجين (27.6 %) السيليكون هو بالتأكيد المادة الأساسية التي ساعدت على دفع الإنسانية من عصر البخار إلى عصر التكنولوجيا و المعلومات والتواصل. في الواقع ، ليس من المبالغة ملاحظة أن السيليكون ليس فقط المادة الأساسية الأكثر دراسة ، ولكنه أيضاً المادة الموجودة في جميع تطبيقات التقنية العالية بدءاً بالإلكترونيات الدقيقة (حديثاً تكنولوجيا الإلكترونيك النانوية) ، تحويل الطاقة الكهروحرارية ، المواد المغناطيسية ، المستشعرات ، النظم الكهروميكانيكية الدقيقة والنانوية بالإضافة إلى تحويل الطاقة الضوئية. في هذا السياق ، من الواضح أن التحويل المباشر للطاقة الشمسية إلى كهرباء هو التكنولوجيا التي تمتلك أكبر إمكانيات التغطية الشاملة لاحتياجات الطاقة المستقبلية. ومع ذلك ، فإن التكنولوجيا لم تصل بعد إلى الكفاءة المثالية و تخفيض التكاليف اللازمة لاعتمادها كمنتوج عام. ومع ذلك ، لا يزال السيليكون هو أنجح مادة لتصنيع الخلايا الشمسية حالياً ، ليس فقط بسبب وفرة و لا لخصائصه الفيزيائية الذاتية ، ولكن أيضاً بسبب التمكن الحاد في تكنولوجيا التصنيع القائمة عليه و المستوحات من الإلكترونيات الدقيقة التي تعتبر بالفعل ناضجة جداً. وتجدر الإشارة إلى أن انخفاض كفاءة التحويل في خلايا السيليكون يرجع في الأساس إلى فجوة الطاقة الغير المباشرة ، وبالتالي التأكيد على أهمية الترتيب الذري للذرات في الشبكة البلورية. ويستند الغرض من هذا الموضوع بشكل أساسي إلى تعديل البنية البلورية للسيليكون على المستوى الذري عن طريق توليف أشكال جديدة من السيليكون تسمى عادة البنية البلورية للسيليكون على المستوى الذري باستخدام صيف و بنيات جديدة تشبه الى حد ما بني الفولرين الصغيرة، و تسمى هذه البنى الجديدة بالكلاثرات . سيتم دعم العمل التجريبي من خلال الدراسات النظرية باستخدام حسابات ميكانيك الكم الأولية كجزء من نظرية الكثافة الوظيفية.

Résumé

Élément le plus abondant sur terre après l'oxygène (27,6%), le silicium est certainement le matériau de base qui a permis de propulser l'humanité de l'âge de la vapeur à l'ère des technologies de l'information et de communication. En effet, il n'est pas exagérer de remarquer que le silicium est non seulement le matériau le plus étudié sur le plan fondamentale mais c'est aussi le matériau qu'on retrouve dans pratiquement dans toutes les applications " High Tech" commençant par la microélectronique (plus récemment la nanoélectronique), la conversion thermoélectrique de l'énergie, les matériaux magnétique, les capteurs, les systèmes micro et nano électromécaniques ainsi que la conversion photovoltaïque de l'énergie. Dans ce contexte, la conversion directe de l'énergie solaire en électricité représente évidemment la technologie qui détient le plus de potentialités concernant la couverture globale des besoins future en énergie. Cependant, la technologie actuelle (principalement à base de Si) n'as encore atteint ni l'efficacité du rendement ni la réduction des couts nécessaires pour son adoption comme produit grand publique. Pourtant, le silicium reste encore le matériau le plus répondu pour la fabrication des cellules solaires, non seulement à cause de son abondance et de ces caractéristiques physiques intrinsèque fondamentales mais aussi à cause de la maitrise pointu de sa technologie de fabrication inspirée largement de la technologie microélectronique déjà très mature. Il faut noter que le faible rendement de conversion du silicium est fondamentalement dû à son gap indirect soulignant ainsi l'importance de l'arrangement atomique des atomes dans le réseau cristallin. Le but du présent sujet, s'articule essentiellement sur la modification de la structure cristalline du Silicium à l'échelle atomique par la synthèse de nouvelles formes de Silicium communément appelées "clathrates" présentant des structures à cages similaires à celles des fullerènes. Le travail expérimental sera appuyé par des études théoriques utilisant des calculs ab-initio dans le cadre de la densité fonctionnel.

