Novel crystal structures for Lithium-Silicon alloy predicted by minima hopping method

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Abstract

We present an *ab initio* study of the phase diagram of the Li-Si binary system using the minima hopping method for global structural prediction. By varying the chemical composition we obtained the theoretical convex hull, whose vertices are constituted by three stoichiometries, two of them have not been reported previously. Additionally, we find five more unreported meta-stable structures, which are slightly higher in energy with respect to the convex hull line. We further characterize all these obtained phases by calculating their electronic, mechanical, and dynamical properties. Finally, and as this class of systems is viewed with interest for possible anodes in lithium batteries, we also report the potential-composition curve and compare it with available experimental measurements.

Keywords: Minima Hopping Method, Li-Si alloys, Li-ion battery, Density functional theory

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1. Introduction

In the past few years, the development of lithium-ion batteries (LIBs) with higher energy capacity has been the focus of many research projects, mainly due to the several potential applications for portable electronic devices and electric vehicles. Lithium-graphite compounds are the most commonly used materials as negative electrodes in LIBs due to their low price, low working voltage, and good energy density. In these compounds, Li atoms are intercalated between the graphite sheets during the charging cycle and removed during discharge with a minimal structural change and a 10% variation in volume [1].

Recently, silicon has been studied as a potential negative electrode in LIBs batteries, primarily because this material has the highest known theoretical storage capacity. The predicted charge capacity is close to 3500 mAh g⁻¹, comparable to graphite, 371 mAh g⁻¹ [2]. However, the lithiation of silicon has been associated with a volume expansion of 300% [3, 4], generating large mechanical strain, and resulting in capacity loss and very limited cycle life [5]. Therefore, it is important to have a clear view of the different crystalline structures of LiSi involved in the process, to understand the causes of this behavior and propose possible solutions.

The stable experimentally reported stoichiometries are LiSi (I41/a, 16 atoms per unit cell), Li₁₂Si₇ (Pnma, 152 atoms),

Li₇Si₃ (P3₂12, 60 atoms), Li₁₃Si₄ (Pbam, 34 atoms), Li₂₂Si₅ (F23, 108 atoms), and Li₂₁Si₅ (F4m3, 104 atoms) [6, 7, 8]. Additionally, a meta-stable crystalline phase of Li₁₅Si₄ (I43d, 38 atoms per unit cell) has been recently reported [9]. This structure does not appear in the normal equilibrium Li-Si phase diagram [10, 11], suggesting that it is possible to obtain novel meta-stable structures under extreme conditions.

From the theoretical side, several methods have recently been used to explore the most stable crystal structures as a function of the stoichiometry, such as genetic algorithms [12] and random search [13]. The crystal structures that were obtained by numerical simulations allowed the construction of theoretical phase diagrams for Li-Si alloys. In particular, Tipton *et al.* [12] predicted a new R3m phase of Li₅Si₂ using density functional theory (DFT) coupled with genetic algorithms. They reported that a supercell obtained from this structure with partial site occupations can represent the Li₇Si₃ structure. Moreover, they found three other unreported stoichiometries (Li₄Si, Li₇Si₂ and Li₉Si₃) for which they only reported the dynamical stability. Chevrier *et al.* [1] demonstrated that Li₂₁Si₅ [8] is chemically more stable than Li₂₂Si₅. Zeilinger *et al.* [14] suggested that Li₁₇Si₄ is the correct stoichiometry between Li₂₂Si₅ and Li₂₁Si₅ at high temperature. Morris *et al.* [13] used *ab initio* random structural search to discover new crystalline phases of LiSi and Li₈Si₃. They found several new phases of LiSi with space groups R3, P4/mmm, P1, P3m1, P2/m and I4₁/amd, which are only 0.05, 0.07, 0.07, 0.07, 0.08 and 0.11 eV per formula unit higher in energy than the ground state structure. For

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$\text{Li}_{17}\text{Si}_4$ they reported a phase with $F\bar{4}3m$ symmetry, for Li_8Si_3 a $R\bar{3}m$ structure and for $\text{Li}_{13}\text{Si}_5$ a $P\bar{3}m1$ structure. Many of the previous theoretical investigations performed an elastic and thermal stability analysis of the predicted structures, in addition to the calculation of the formation enthalpy.

In this work, we use the minima hopping method (MHM) proposed by Goedecker [15, 16] to investigate the binary phase diagram of Li-Si at zero pressure. The article is organized as follows. In section 2, we describe the computational details of our calculations. Section 3 discusses the crystal structures obtained for all the different compositions, with a particular focus on those on the convex hull or very close to it. After selecting the lowest enthalpy structures, we perform an electronic, mechanical and dynamical characterization to describe general thermodynamic properties. We end section 3 by discussing the potential-composition curve of Li-Si binaries as a function of Li content. Section 4 summarizes our work.

2. Computational details

Different numerical approaches can be used nowadays to sample the potential energy surface in order to find the global energy minimum. In this work, we use the minima hopping method (MHM) for global structural prediction. This method employs an efficient dynamical algorithm to explore the energy landscape by using temperature as a key variable to overcome the potential barriers and reach lower minima. When coupled with *ab initio* density functional theory (DFT), this method is capable of predicting stable and meta-stable crystal structures at a given pressure, from the sole knowledge of the chemical composition of the system. A series of consecutive short molecular dynamics (MD) simulations are used to escape from a local minimum by overcoming an energy barrier. We perform NPT MD simulations with a time interval of 700 fs (3.5 fs time step) and an initial temperature of 200 K, which is potentially increased with a factor of 1.2 according to the algorithm. It is this temperature change the one responsible for the necessary energy to overcome energy barriers. After the MD simulation, local geometry relaxation is performed to identify the configuration corresponding to the new energy valley bottom. The efficiency of the escape step is improved by choosing the initial velocities of molecular dynamics trajectories approximately along of soft mode directions [15].

For the structural search calculations presented in this paper, we used unit cells containing up to 16 atoms and considering all possible stoichiometries under this restriction. The evaluation of energy and forces required for MHM were obtained from DFT as implemented in the Vienna Ab initio Simulation Package (VASP version 5.3.3) [17, 18]. The projected augmented wave (PAW) method was used to describe valence and core electrons [19]. In this case the electronic configurations taken into account in the PAW pseudo-potential were: five valence electrons for Li ($1s^2 2s^2 2p^1$) and four for Si ($3s^2 3p^2$). To approximate the exchange-correlation functional of DFT, we used the Perdew-Burke-Ernzerhof (PBE) [20] generalized gradient approximation. We used a plane wave cutoff of 550 eV, and a

Monkhorst-pack [21] method (Gamma-center k -grid for hexagonal and trigonal structures were used). Brillouin zone sampling grid was converged to guarantee a numerical accuracy of the total energy to less than 2 meV/atom. In order to ensure the dynamical stability of the identified crystal structures, we calculated their phonon dispersion. The software PHONOPY [22] was used to obtain the force constants from VASP with a $2 \times 2 \times 2$ supercell. Elastic constants which converged to less than 1 GPa were calculated from strain-stress relations as implemented in VASP. For the calculations of the elastic and electronic properties, k -point grids of size $12 \times 12 \times 12$ were used.

An important observable related to lithium batteries is the electric potential profile. The experimentally reported profiles show the open circuit voltage of a battery as a function of the anode lithium content. The average cell potential can be calculated under the assumption of a two-phase reaction from reactant to product [6, 23, 24].

where the average voltage is defined as

$$\text{Voltage} = - \left\{ \frac{G_{\text{Li}_y\text{Si}} - G_{\text{Li}_x\text{Si}}}{y - x} - G(\text{Li}_{\text{metal}}) \right\}$$

with the Gibbs free energy G defined as

$$G = E + pV - TS$$

Where E is energy, V is volume, p is pressure, T is temperature, and S is entropy. In this case, the pV contribution to G is of the order of $10 \mu\text{eV}$ per Li at atmospheric pressure [25]. The TS contribution to the voltage is assumed to be constant and estimated to be on the order of 10 meV [25, 26]. Therefore, the average potential of the electrode can be derived from the simple equation:

$$\text{Voltage} = E(\text{Li}) - \frac{E(\text{Li}_y\text{Si}) - E(\text{Li}_x\text{Si})}{y - x}$$

Here, we have calculated total energies (or enthalpies) by means of electronic structure calculations within DFT.

3. Results and Discussion

We studied sixty different stoichiometries of the Li-Si system, starting from pure silicon up to pure lithium. For each stoichiometry, a structural search was performed as described in section 2. Then, the lowest energy structures were identified and selected for structural re-optimization with a tighter stress and force convergence criteria.

Combining the calculated formation energies for all different stoichiometries, we have calculated the theoretical convex hull as depicted in Fig. 1. The thermodynamically stable structures are indicated with (black) circles and define the vertices of the convex hull (black line). Low-lying local minima are represented by (magenta) crosses. Additionally, we also construct the convex hull (red dashed line) associated with the experimental structures. These structures were available through

Figure 1: Convex hull of the lithium-silicon binary system. The black continuous line is obtained from *ab initio* MHM calculations, and black circles indicate thermodynamically stable structures. The red dashed line is the convex hull constructed from the formation energy of experimental structures (red diamonds). The blue dashed-dotted line and green dotted line are the convex hulls constructed with the formation energies (blue star and green triangle symbols) of the structures reported by Morris *et al.* [13] and Tipton *et al.* [12], respectively.

the materials project [27] and OQMD [28] databases. Note that the experimental structures were also relaxed using VASP and using the same functional and convergence criteria as the ones obtained from our structural search. The (blue) dashed-dotted line with (blue) stars corresponds to the predicted convex hull obtained by Tipton *et al.* [12], and the (green) dotted line with (green) triangles was calculated by Morris *et al.* [13]. By inspection of Fig 1, we see that our theoretical hull lies above the experimental structures of $\text{Li}_{12}\text{Si}_7$, Li_7Si_3 , $\text{Li}_{13}\text{Si}_4$, $\text{Li}_{22}\text{Si}_5$, $\text{Li}_{21}\text{Si}_5$ and $\text{Li}_{15}\text{Si}_4$. There is an easy explanation for that: the experimentally determined crystal unit cells contain a large number of atoms compared to our maximum number of 16 atoms. More specifically, the unit cells of the above listed compositions contain 152, 60, 34, 108, 104, and 38 atoms, respectively [29, 1]. A summary of the number of atoms per unit cell for all structures reported in this work can be found in Table 1.

We emphasize that our methodology consistently reached crystal phases at a lower energy than those previously reported by Tipton *et al.* [12] and Morris *et al.* [13]. These authors also used DFT to determine energies and forces, and with the same exchange-correlation functional. However, the genetic algorithm employed by Tipton *et al.* is interfaced with VASP, while Morris *et al.* relied on CASTEP [13] for their random

search. It is not clear from where the observed discrepancies come. Even though different implementations have been used, it is expected that energy differences should be closer as compared with different calculations within the same exchange correlation functional. Therefore, we can only suggest that it could be due to different convergence criteria and the methodology used.

We do note that for the case of Li_5Si_2 , one of the key results in the works of Tipton *et al.* [12] and Morris *et al.* [13], we find good agreement with respect to the predicted symmetry group, lattice parameters and Wyckoff positions. However, we find a small energy difference between our calculated formation energy and the ones reported by Tipton *et al.* [12] and Morris *et al.* [13], 11 meV and 22 meV respectively, with our structure lower in energy, a difference that could be due to the used methodologies.

Several unreported phases are characterized for the first time in our work. In fact, our MHM runs have identified two new phases for Li_3Si (space group $P12/m1$) and Li_4Si (space group $I4/m$), which are on the theoretical hull and have not been previously reported. Additionally, we found novel low-energy meta-stable structures for Li_3Si_2 (space group $C12/m1$), Li_2Si (space group $C12/m1$), Li_9Si_4 (space group $C12/m1$), Li_7Si_2 (space group $P\bar{3}m1$), Li_5Si (space group $P\bar{3}m1$) and

Table 1: All experimental and theoretical Li-Si phases studied in this work. Experimental phases from Refs. [1, 29].

Phase	space group	number of atoms
Experimental		
$\text{Li}_{12}\text{Si}_7$	$Pnma$	152
Li_7Si_3	$P3_212$	60
$\text{Li}_{13}\text{Si}_4$	$Pbam$	34
$\text{Li}_{22}\text{Si}_5$	$F23$	108
$\text{Li}_{21}\text{Si}_5$	$F\bar{4}3m$	104
$\text{Li}_{15}\text{Si}_4$	$I\bar{4}3d$	38
This work		
Li_5Si_2	$R\bar{3}m$	7
Li_3Si	$P12/m1$	12
Li_4Si	$I4/m$	5
Li_7Si_2	$P\bar{3}m1$	9
Li_3Si_2	$C12/m1$	10
Li_2Si	$C12/m1$	12
Li_9Si_4	$C12/m1$	13
Li_5Si	$P\bar{3}m1$	12
Li_6Si	$R\bar{3}m$	7

Li_6Si (space group $R\bar{3}m$) which are very close to the convex hull (only 4, 3, 5, 2 and 4 meV/atom, respectively). These energy differences are on the order of the numerical accuracy of our theoretical description. Moreover, meta-stable structures close to the convex hull could be easily stabilized experimentally by temperature, pressure, or doping. We want to stress that for some compositions we find a large set of low-energy structures close to the convex hull. This implies that for those stoichiometries the system has available many different possibilities to crystallize which could lead to the amorphization of the general structure, or the coexistence of regions of different phases, as it is also observed experimentally.

In Table 2 we summarize the crystallographic information for the crystal structures belonging to the theoretical convex hull, as well as for the most interesting meta-stable structures. The atomic arrangement that we obtained for Li_3Si_2 , Li_2Si , Li_9Si_4 , Li_5Si_2 , Li_3Si , Li_7Si_2 , Li_4Si , Li_5Si and Li_6Si are further displayed in Fig. 2. Complete crystallographic information for all structures can be found in the supplementary information. We observe a large diversity of atomic configurations. In the case of Li_3Si_2 , we can see that Si atoms form an armchair chain, while in Li_2Si they form zig-zag chains. In Li_9Si_4 , Si dimers appear surrounded by Li atoms, and a similar arrangement is finding in Li_5Si_2 . In the case of Li_3Si , we note the formation of Si dimers, but now we see isolated Si atoms surrounded by Li atoms. This bonding has similar a pattern as in the experimental structures [1, 13], where for example, we observe the formation of Si dimers in Li_7Si_3 , and $\text{Li}_{13}\text{Si}_4$. In $\text{Li}_{15}\text{Si}_4$, $\text{Li}_{21}\text{Si}_5$, and $\text{Li}_{22}\text{Si}_5$ we can see the Si atoms become electronically isolated and surrounded by Li atoms. A similar behavior is observed in our structures.

The different arrangements can be further characterized by comparing their electron localization functions (ELF), as depicted in Fig. 3. In the case of Li_3Si_2 we can observe the lo-

calization of the electrons resulting in bonding between Si-Si. But, with the increase of Li content, we see the electrons start to delocalized, increasing the metallicity. In Li_3Si , we can see the charge transfer between Si-Si and isolated Si surrounded by Li, resulting in electron delocalization. The same happens for the isolated Si atoms in Li_4Si . A similar observation holds for Li_5Si , but in this case there is also a electron delocalization between Li layers. Therefore, we can observe that with the increase of Li content the electrons are more delocalized, resulting in a metallic character of the binary compound.

Figure 4: Total and local density of states per f.u. for (a) Li_5Si_2 (trigonal, $R\bar{3}m$), (b) Li_3Si (monoclinic, $P12/m$), and (c) Li_4Si (tetragonal, $I4/m$). Red and blue line are the s -orbital projections of Li while green and pink are the p -orbital projections of Si.

The Fig. 4, shows the total and local density of states (DOS) normalized per formula unit (f.u.) for the structures in the convex hull (the DOS for the meta-stable structures are reported in the supplementary information), it is clear that the structures have a predominantly metallic character, with a significant density of states at the Fermi energy. In general, we can see that most of the metallic character is coming from the Si- p orbitals. The exception is Li_5Si and Li_6Si , where now the lithium content is so large that it plays a similar role as the p orbitals from Si. For the case of Li_6Si , the total density of states at the Fermi

Figure 2: Crystal structure of (a) Li_3Si_2 (monoclinic, $C12m/1$), (b) Li_2Si (monoclinic, $C12m/1$), (c) Li_9Si_4 (monoclinic, $C12m/1$), (d) Li_5Si_2 (trigonal, $R\bar{3}m$) (e) Li_6Si (trigonal, $R\bar{3}m$) (f) Li_3Si (monoclinic, $P12/m1$), (g) Li_4Si (tetragonal, $I4/m$), (h) Li_7Si_2 (trigonal, $P\bar{3}m1$) and (i) Li_5Si (trigonal, $P\bar{3}m1$). Li atoms are green while Si atoms are blue.

Table 2: Lattice parameters, angles, and space group for the lowest-energy meta-stable structures.

Phase	space group	a	b	c	α	β	γ
Li_5Si_2	$R\bar{3}m$	4.387	4.387	17.862	90	90	120
Li_5Si_2 [12]	$R\bar{3}m$	4.383	4.383	17.837	90	90	120
Li_3Si	$P12/m1$	6.487	4.311	6.385	90	103.19	90
Li_4Si	$I4/m$	5.952	5.952	4.292	90	90	90
Li_7Si_2	$P\bar{3}m1$	4.375	4.375	7.958	90	90	120
Li_3Si_2	$C12/m1$	12.217	4.368	6.147	90	75	90
Li_2Si	$C12/m1$	12.232	4.410	7.937	90	90	120.61
Li_9Si_4	$C12/m1$	12.283	4.38	7.534	90	78.12	90
Li_5Si	$P\bar{3}m1$	4.437	4.437	11.061	90	90	120
Li_6Si	$R\bar{3}m$	4.448	4.448	19.995	90	90	120

level corresponds to the largest of all considered cases, close to 1.2 states/eV/f.u. Additionally, the full band structure for each case has been included in the supplementary information.

It is well-known that the existence of imaginary frequencies in the phonon spectra indicates that the system is not dynamically stable. In Fig. 5 we present the phonon band structure of Li_5Si_2 , Li_3Si , and Li_4Si . The phonon band structure of the meta-stable structures are also included in the supplementary information. We clearly observe that all phonon frequencies are positive, whence unstable modes are not present. For many structures all acoustic branches have almost the same slope, indicating the isotropic elastic behavior of the material, while in a few cases large differences exist between the different branches. In order to analyze the effect of the variation of Li content on the thermodynamic properties of the materials, we report in Fig. 6 the vibrational contribution to the heat capacity. The peak on the heat capacity (normalized to T^3) expresses the amount of

thermal energy one can acquire. Even though a certain dependence is noticed (the change in the thermal energy tends to be higher for higher lithium content), we are not able to find a clear tendency. Indeed, the maximum value is quite dependent not only on the Li content but also on the crystal structure.

We now turn our attention to the elastic properties. In the context of Li batteries, the mechanical properties are important because they are relevant for the possible anode deformation. Usually, the change in the volume during a charge and discharge process (lithiation/delithiation) can result in mechanical failure due to cracking or pulverization of the electrode [30, 31, 32]. In order to characterize the elastic behavior of these binary compounds we calculated the bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (ν) for a polycrystalline material. These quantities can be obtained from the single crystal elastic stiffness constants C_{ij} , using the Voigt-Reuss-Hill approximation [33], which can be

Figure 3: Electron localization function (ELF) of (a) Li_3Si_2 (monoclinic, $C12/m1$), (b) Li_9Si_4 (monoclinic, $C12/m1$), (c) Li_3Si (monoclinic, $P12/m1$), (d) Li_4Si (tetragonal, $I4/m$), (e) Li_5Si (trigonal, $P3m1$). Li atoms are green while Si atoms are blue. In the scale color 0.0 corresponds to localization of electrons and 1.0 corresponds to delocalization of electrons.

Figure 5: (a) Phonon band structures of (a) Li_5Si_2 ($R3m$), (c) Li_3Si ($P12/m$), and (g) Li_4Si ($I4/m$).

Figure 6: Vibrational contribution to the heat capacity for the lowest-energy structures reported in this work.

expressed as follows:

$$B = \frac{1}{2}(B_V + B_R) \quad G = \frac{1}{2}(G_V + G_R) \quad (1)$$

with

$$9B_V = (C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{13} + C_{23}) \quad (2a)$$

$$15G_V = (C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23})) \quad (2b)$$

$$1/B_R = (s_{11} + s_{22} + s_{33}) + 2(s_{12} + s_{23} + s_{31}) \quad (2c)$$

$$15/G_R = 4(s_{11} + s_{22} + s_{33}) - 4(s_{12} + s_{23} + s_{31}) + 3(s_{44} + s_{55} + s_{66}), \quad (2d)$$

where $C_{ij}=1/s_{ij}$. When B and G have been determined, E and ν can be easily calculated using:

$$E = \frac{9BG}{3B + G} \quad \nu = \frac{3B - 2G}{2(3B + G)}. \quad (3)$$

Table 4: Calculated Bulk (B), shear (G), Young (E) modulus in GPa, Poisson's ratios (ν) and B/G ratios.

Phase	B	G	E	ν	B/G
Si	89.5	62.7	152.9	0.22	1.4
Si exp [9]	97.6				
Si ref[5]	88.32	64.91	156.13	0.19	1.4
Li ₃ Si ₂	38.4	29.1	69.7	0.19	1.3
Li ₂ Si	37.8	29.1	69.4	0.19	1.3
Li ₉ Si ₄	37.1	31.2	73.0	0.17	1.2
Li ₅ Si ₂	39.8	34.8	79.8	0.16	1.1
Li ₃ Si	35.9	30.7	71.2	0.17	1.2
Li ₇ Si ₂	33.9	27.5	64.7	0.18	1.2
Li ₄ Si	29.7	26.6	60.7	0.16	1.1
Li ₅ Si	26.5	18.0	43.3	0.22	1.5
Li ₆ Si	23.9	16.1	39.0	0.22	1.5
Li	14.1	6.7	17.5	0.3	2.1
Li exp[38]	12.13	8.78	21.22	0.21	1.38
Li ref[5]	13.61	10.01	37.96	0.14	1.35

Table 3 presents the elastic constants of all phases here reported. Likewise, in Table 4 we summarize the bulk, shear, and Young modulus as well as the Poisson's ratio and the B/G ratio for the phases reported and for the pure elements (Li and Si). It is well known that the ration B/G can be used to classify brittle and ductile behavior in materials [34, 35]. We can observe that the bulk modulus decrease monotonically with the increase of the Li content, while Young's Modulus is constant up to 71% of Li, before beginning to decrease. B/G ratios smaller than 1.75 are associated with brittle alloys, while values larger than 1.75 with ductile materials. Looking at our structures, we can see that B/G is smaller than 1.75, suggesting that all structures are brittle. This observation is in agreement with those reported by J. Xia *et al.* [36]. With the increase of Li content, the presence of covalent bonds decreases and the presence of metallic bonds increases due to the electron delocalization, making the whole structure weaker. A further confirmation comes from the determination of the Cauchy pressure, which is estimated from the difference between C_{12} and C_{44} (if it is negative, the crystal tends to be brittle). The phase having highest Li content in this work is Li₆Si and its bulk modulus is smaller than the value for Si by almost one order of magnitude. This behavior clearly suggests an elastic softening and mechanical failure in phases with high Li content and an overall strong dependency of the mechanical properties on Li concentration. We note that our results are in qualitative agreement with those related to experimental phases [5, 37, 32].

Figure 7 shows the electric potential profile as a function of Li content for the structures belonging to our theoretical convex hull. The voltages were calculated as previously described in section 2. We also compare our calculated potential profile with the experimental one reported at 415 °C by Wen *et al* [6]. We can see a similar behavior in the electric potential as a function of the Li content using our structures, despite the fact that we do not include temperature effects. Our electric potential profile is in agreement with those experimentally and theoreti-

Figure 7: Electric potential profile of Li-Si alloys as a function of the Li content compared with the profile calculated using experimental structures.

cally reported [12, 13, 1].

4. Summary

In summary, we report a set of new crystal structures for Li-Si binary compounds obtained by using the minima hopping method, and by varying the chemical composition. In order to understand the electronic properties of these compounds, we have calculated the density of states and electron localization functions. We find that the structures are mostly metallic, with metallicity increasing with the lithium content. Additionally, we verified the dynamical stability of all considered structures by calculating the phonon spectra. We further characterized the elastic properties by determining the bulk modulus, shear modulus, Young modulus, and Poisson's ratio. We observed that mechanical properties, phonon dispersion, and electron localization functions are strongly sensitive to the Li content and depend on the nature of the bonds. We finally calculate the electric profile as a function of the Li content, finding an overall agreement with data in literature.

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Table 3: Computed elastic constants for Li-Si binaries here reported. All quantities are in units of GPa.

	Li ₃ Si ₂	Li ₂ Si	Li ₉ Si ₄	Li ₅ Si ₂	Li ₃ Si	Li ₇ Si ₂	Li ₄ Si	Li ₅ Si	Li ₆ Si
C ₁₁	125.3	110.0	124.6	102.1	78.4	85.9	49.0	73.4	61.7
C ₁₂	13.9	2.4	3.8	16.6	-2.7	17.9	24.1	10.2	7.1
C ₁₃	12.3	19.1	1.7	-9.7	33.8	3.0	13.0	2.5	8.7
C ₁₄				-15.6		-12.2		11.9	-10.7
C ₁₅	0.7	-15.8	-1.6		-5.4				
C ₁₆							-20.9		
C ₂₂	85.8	82.1	85.5	102.1	89.5	85.9	49.1	73.4	61.7
C ₂₃	3.4	19.4	17.0	-9.7	22.7	3.0	13.0	2.5	8.7
C ₂₅	-0.8	-5.8	-6.9		1.1				
C ₃₃	84.1	69.7	81.4	162.1	49.3	86.5	70.4	63.1	43.6
C ₃₅	-1.1	12.7	6.1		-4.9				
C ₄₄	14.9	35.1	30.1	24.0	48.5	22.1	32.9	11.9	12.4
C ₄₆	2.5	-1.9	-6.4		-2.7				
C ₅₅	33.1	36.1	23.2	24.0	58.7	22.1	32.9	11.9	12.6
C ₆₆	22.9	16.4	24.6	42.8	21.9	33.9	36.1	27.3	27.3

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