Exploring silicon allotropy and chemistry by high pressure –
high temperature conditions.

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Abstract. Silicon is the second abundant element, after oxygen, in the earth crust. It is essential
for today’s electronics because of its ability to show various electronic behaviors that allow
covering the numerous fields of cutting-edge applications. Moreover, silicon is not a pollutant
and, therefore, is an ideal candidate to replace the actual materials in photovoltaics, like
compounds based on the arsenic and heavy metals. It has not replaced them so far because Si is
an indirect gap semiconductor and cannot absorb directly the solar photons without thermal
agitations of crystal lattice (phonons). This puts it apart from the next-generation applications
(light diode, high-performance transistor). That justifies the attempts to create silicon materials
with direct gap that can absorb and emit light. Our recent high-pressure studies of the chemical
interaction and phase transformations in the Na-Si system, revealed a number of interesting
routes to new and known silicon compounds and allotropes. The pressure-temperature range of
their formation is suitable for large-volume synthesis and future industrial scaling. The variety
of properties observed (e.g. quasi-direct bandgap of open-framework allotrope Si₃₄) allows us
to suggest future industrial applications.

1. Introduction
During last years high pressure techniques have been widely used for creation of new solids with
advanced mechanical and physical properties [1]. High pressure completely change the
thermodynamics and chemistry of elements, known at ambient pressure [2], and allowed obtaining
novel (i) crystal structures, (ii) compositions and even (iii) nanostructures. Detailed characterization
of these materials have been performed by physical measurements and thermodynamic analysis [3].
For some solids, the whole of properties allows considering them as advanced superhard,
semiconductive and even photovoltaic materials. The pressures required for synthesis of many of them
belong to the domain easily accessible for industrial scaling (up to 2500 K and 10 GPa).
High pressure often induces new allotropy in the elements [4]. However, most of the crystal
structures that form under extreme pressure-temperature conditions cannot be recovered at ambient.
Those that remain metastable, can be potentially considered as new materials, similar to synthetic
diamond. Recent discoveries of two novel boron allotropes, orthorhombic γ-B₂₈ [5,6] and tetragonal
(pseudo-cubic) pc-B52 [7], allowed us to construct the boron phase diagram, which has been questioned for more than one century [8], but also considering boron as superhard, second only after carbon in its diamond form(s) [9].

High pressure also completely changes element chemistry. For example, magnesium and carbon, both of which form numerous compounds with other elements, have remarkably low affinity to each other. At ambient pressure, only the reaction of Mg or MgO with hydrocarbons leads to the formation of metastable carbides with reasonable yields, and pure Mg and carbon do not react to form stable compounds at any temperature. It has been demonstrated that under high-pressure conditions (above 5 GPa and 1300 K) thermodynamically stable Mg-C compounds are possible. The new compound synthesized, $\beta$-Mg$_2$C$_3$ [10], crystallizes in the monoclinic $C2/m$ space group, and contains rare allylene-derived $C_3^{\text{allyl}}$ anions that are isoelectronic with $\text{CO}_2$. At higher pressures, above 15 GPa, antifluorite Mg$_2$C forms [11].

The application of high pressure for materials synthesis, both in industry and science, have been traditionally limited to superhard materials [14,15], e.g. diamond [16,17], cubic boron nitride cBN [18,19], carbon-metal systems [20], including Mg-C described above [13], nano-cBN [21], nanodiamond [22], cBC$_n$ [23,24], $\gamma$-B$_{25}$ [5,6,25], B$_{13}$N$_2$ [26-31], B$_6$O [32-35], high-pressure B$_2$O$_3$ [36-38], etc. Some interest has been paid to design [39,40] and understanding [41-43] of high-pressure superconductors. Our recent results allowed us to overcome this "restriction" and to give a new dimension for design of high-pressure materials. Silicon is essential for today’s electronics because of its ability to show various electronic behaviors that allow covering the numerous fields of cutting-edge applications, in particular in optoelectronics. For this reason many attempts have been made to design a silicon with direct gap that could efficiently absorb and emit light. Ideal material should have optically allowed direct bandgap [44], close direct & indirect gaps of absolute values from 1 to 2 eV in order to have highest efficiency of cells, and high light absorption in thin films [45,46].

### 2. Synthesis of dense tetrahedral silicon allotropes

Seven dense (i.e. without large voids) crystal structures of Si are known to be stable at pressures from 1 MPa up to 100 GPa at room temperatures [53-58]; and three more phases are believed to be metastable below 10 GPa [59,60]. At ambient conditions one can recover only Si-I (common and most stable diamond structure) [53], and two metastable Si-III and Si-IV [59]. The crystal forms that exist below 16 GPa have tetrahedral coordination (from ideal in diamond Si-I and lonsdaleite Si-IV) [53,59,61] to strongly distorted (white-tin Si-II and orthorhombic Si-XI [54,58]). Above 16 GPa the stable crystal structures are produced mainly by traditional hexagonal or cubic packing (hp Si-V, hcp Si-VII and cccp Si-X [55,56]).
Figure 1 shows the relative transformations at pressures below 12 GPa. Only three phases can be obtained/recovered at ambient conditions. In the case of diamond silicon (Si-I) the bandgap engineering by nanostructuring [62] is possible. However, the most interesting is exotic Si-III (BC8) phase. In a pure polycrystalline state (with strained lattice) it can be obtained by decompression from above 15 GPa without heating [63] or from pressures above 10 GPa with heating [64]. It is a semimetallic allotrope, whose gap was predicted to open by (1) the change of structural order parameter, the $x$ of Wickoff position 16c with ($x,x,x$) unit cell coordinates in $Ia-3$ space group (No 206) [65], or (2) the grainsize of Si-III clusters [66]. Moreover, very recently the nanoparticles of BC8 cubic silicon obtained by a mean of colloidal chemistry were claimed in ref. [67]. The bandgap measured by absorption in visible region was found to be of ~2.8 eV [67], slightly higher than predicted by ab initio calculations for the same grainsize [66].

Our recent results on Na-Si interactions at HPHT conditions using large-volume multianvil press and synchrotron radiation at the ID06 beamline of the ESRF, have indicated the possibility to obtain pure polycrystalline strain-free Si-III grains up to 500 μm at pressures as low as 9.5 GPa in the Na-Si system. At lower pressure this phase was also often observed (at least down to 7 GPa in Na-Si system), but pure grains cannot be easily extracted. In a number of samples obtained in our experiments by variation of chemical conditions, Rietveld refinement give $x$ from 0.101 to 0.105. The lowest $x$ corresponds to the sample obtained at room temperature (~13 GPa in our experiments using Paris-Edinburgh cell at IMPMC, 40% yield of Si-III). At the same time the nanoparticles [67], the PXRD pattern may be adjusted to original cubic $Ia-3$ space group using structureless full-profile LeBail analysis, however the pattern shows quite different intensities from theoretical ones. Our attempts to adjust the intensities to experimental one using Rietveld analysis, led to the value of $<x>$ as low as of ~0.088. However, not all the intensities are in reasonable agreements, moreover, very short Si-Si bonds appear (17% shorter as compared to expected ~2.4 Å). To avoid these discrepancies, we tried to refine the structure using cubic subgroups of $Ia-3$ space group. The obtained mean values of $x$'s are between 0.070 and 0.088, representing the analogue of $x$ in the original structure, now for 2 or 4 sublattices of Si with more reasonable interatomic distances. More detailed study of this crystallographic point is required. Anyway, one can easily see the possibility of vary $x$ by the methods of synthesis. Here, the grainsize may be considered a crucial point for impact on order parameter $x$ (or $<x>$) and even stability of crystal structure, different from microcrystalline bulk counterpart, like it often occurs, e.g. for nano polymorphism of TiO$_2$ [68] or stability of nanostructured high-pressure form of ZnO [69,70].

![Figure 1](image1.png)

**Figure 1.** Direct phase transformations between dense Si forms.

![Figure 2](image2.png)

**Figure 2.** Bandgap of Si-III (BC8) as a function of order parameter, atomic coordinate ($x,x,x$).
Figure 2 shows the relative position in the order parameter $x$ - bandgap $E_g$ coordinates of Si-III nanoparticles [67] vs polycrystalline materials synthesized at high-pressure by direct transformation & in chemical systems (Na-Si in our case). Solid line connect the $ab \ initio$ points [65] (open circles); although the “extrapolated values” may be quite different from true $ab \ initio$ values, the general tendency of gap opening with decreasing $x$, is expected with quite high probability. The experimentally known materials are represented by large red circles (denoted micro and nano, the size of the red circles approximatively represent the spread/error of experimental values). One can see that, although displaced, the experimental and $ab \ initio$ dependencies of bandgap on $x$ (or <$x>$) have very similar slopes (here we can note that usually DFT calculations often lead to underestimated band gap values, which give even more relevance to the tendency shown on Figure 2). So, now semimetallic polycrystalline and semiconductive wide-bandgap semiconductive nanoparticles are known for Si-III.

The use of high-pressure chemical reactions seem to be quite promising to fulfill the “gap” of materials with intermediate (direct) bandgaps (especially close to 1-2 eV) by playing the grainsize through the kinetics dependent on $p$-$T$-time regime and chemical environments.

3. Synthesis of open-framework silicon allotropes

As it has been already mentioned above, high-pressure is a newly proposed route to the new and known compounds in the Na-Si system [51,71] (Zintl phase Na$_8$Si$_4$ and intermetallic clathrates Na$_6$Si$_{16}$, Na$_{24+x}$Si$_{136}$ and Na$_4$Si$_{24}$); while the pressure-temperature range of their formation (3-8 GPa) is suitable for large-volume synthesis and future industrial scaling. Moreover, sodium removal at $T > 700$ K from the common Na$_{24-x}$Si$_{136}$ [72] or its high-pressure form Na$_{24+x}$Si$_{136}$ leads to the “clathrate” allotrope Si$_{136}$ with quasidirect bandgap [73] of ~2 eV [74] (Figure 3). Unfortunately, the direct electron transitions at $\Gamma$ point are not allowed by the cubic symmetry and this silicon form is not a good candidate for photovoltaic applications.

In a similar way, sodium removal from Na$_4$Si$_{24}$ by heating in vacuum leads to a new allotrope of silicon with zeolite structure, orthorhombic o-Si$_{24}$ [75] (Figure 3). In this case the required temperature is remarkably lower, ~400 K. The zeolite silicon framework deform during this process (+6% along $a$-axis and -3% along $b$- and $c$-axes), but in general silicon structure remain the same (zeolite CAS). The quasi-direct bandgap of ~1.3 eV with allowed direct electronic transitions due to orthorhombic symmetry ($Cmcm$ space group) allow considering this material for future photovoltaic applications.

![Figure 3](image3.png)

**Figure 3.** Chemical routes to clathrate silicon allotropes. Top: Synthesis below 0.1 MPa (in Ar or vacuum) [71], bottom: combined synthesis at ~8 GPa (Na$_8$Si$_4$+Si) and in vacuum [51,75].

4. Hardening of silicon clathrates

Silicon clathrates seem to have the most rigid covalent framework as compared to other clathrates (with frameworks produced by other elements of group 14, silicon oxide or water), since carbon...
clathrates are not known at present time [79]. So they are the hardest known clathrates with highest elastic moduli, including bulk modulus. In particular, the hardness, just like the bulk modulus and other elastic constants, is expected to be close to that of conventional diamond silicon Si-I [73], even in the case of empty-case Si$_{136}$. The rigidity of silicon framework is defined by Si-Si bondings, and both intercalated metals and voids does not influence it much.

Only one compound known experimentally can be a candidate to be harder than silicon clathrates, i.e. K$_7$B$_7$Si$_{39}$ [80]. Here the B atoms replace Si the clathrate framework and one may expect that hardness should become higher than in the case of Si frameworks, expected value of $H_v$ $\sim$10 GPa [76], although still lower than in the case of boron ($H_v$ > 40 GPa) [9,78]. The hardness estimations (in this chapter we talk about the limit Vickers hardness value in the high-load limit [76]) by modelling is not a trivial, but is still possible task. To do that, one may suggest - similarly to the case of known clathrates - the mechanical properties are close to the original diamond phase of the framework element(s). This was confirmed for Si clathrates (e.g. in the experiments on compressibility measurements [81,82]) and predicted for hypothetical carbon clathrates (both carbon [73,82] and carbon-boron frameworks [83]), expected to have the highest hardness among the clathrate family.

Our previous estimations of a number of B-Si phases indicated that most compounds are at the lower boundary of superhardness (conventionally, 40 GPa of Vickers hardness $H_v$ for cubic boron nitride, second hardest material after diamond on industrial scale). The good correlation of previous estimations using “thermodynamic model of hardness” [77] that typically gives 10% accuracy for a large number of covalent and partially ionic compounds. Our estimates give a value of $H_v$ $\sim$20 GPa for K$_7$B$_7$Si$_{39}$ [80] (strictly speaking, for “B$_8$Si$_{38}$” clathrate framework, Figure 4), which should exceed that of silicon nitride Si$_3$N$_4$ and lays between diamond silicon Si-I and industrial abrasive silicon carbide SiC. In the case of recently predicted Li-B-C clathrates [83], the hardness should be close to that of diamond-like cBC$_x$ phases [24] (Figure 4). The detailed study of the interstitial-atom impact on hardness of clathrates (both of intercalated and Zintl nature) outstand the scope of present work.

5. Conclusions
Finally, chemical interactions in the Na-Si system are very promising for elaboration of known (Si-III or BC8) or new (zeolite o-Si$_{24}$) allotropes of silicon in the forms of well crystallized polycrystalline grains of high purity. High pressure chemical routes seem also quite promising, by varying $p$-$T$-time-concentration protocols for nanostructuring & bandgap engineering, however, unexplored so far. The improvement of mechanical properties of Si framework (and of clathrate in total) is also possible by silicon replacement for boron.

Acknowledgements
The high-pressure syntheses using in situ X-ray diffraction were performed at ID06 beamline at the European Synchrotron Radiation Facility (Grenoble, France). We thank B. Baptiste for help in high-temperature studies of clathrate and allotrope stability in vacuum.

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