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Phase boundary between Na–Si clathrates of structures I and II at high pressures and high temperatures

Understanding of the covalent clathrate formation is a crucial point for the design of new superhard materials with intrinsic coupling of superhardness and metallic conductivity. It has been found that silicon clathrates have the archetype structures, which can serve an existent model compounds for superhard clathrate frameworks Si–B, Si–C, B–C and C with intercalated atoms (e.g., alkali metals or even halogens) that can assure the metallic properties. Here we report our in situ and ex situ studies of high-pressure formation and stability of clathrates Na_8Si_{46} (structure I) and $Na_{24+x}Si_{136}$ (structure II). Experiments have been performed using standard Paris–Edinburgh cells (opposite anvils) up to 6 GPa and 1500 K. We have established that chemical interactions in the Na–Si system and transition between two structures of clathrates occur at temperatures below silicon melting. The strong sensitivity of crystallization products to the sodium concentration has been observed. A tentative diagram of clathrate transformations has been proposed. At least up to ~ 6 GPa, $Na_{24+x}Si_{136}$ (structure II) is stable at lower temperatures as compared to Na_8Si_{46} (structure I).

Keywords: silicon clathrates, superhard clathrates, phase diagram, high-pressure synthesis.

The techniques of high pressure and high temperature (HPHT) appear to be the tools of choice for the synthesis of novel superhard [1, 2] and other useful materials [3] with optimized properties. Although such synthesis usually leads to the significant decrease of the reaction volume, (1) the strong changes of crystal chemistry [4, 5], chemical reactivity [6–8], crystallization, and growth rate

[9], chemical thermodynamics [10–13] and thermophysical properties [14, 15]; and (2) the possibility of direct interactions of components [7], direct phase transformations [16], and nanostructuring [17] allow the consideration of this method as promising for future materials science [18–21], outside traditional limit of diamond and boron nitride materials.

The modern design of advanced superhard materials is often based on the phases with crystal structures typical for elements of the second period (diamond, boron, and borides) [1, 2, 4, 5, 16, 17]. At the same time, the theory predicts the superhard frameworks B–C and C that have crystal structures more typical for larger analogues, for example, for silicon compounds (e.g. clathrates, zeolites). With intercalated atoms (e.g., alkali metals or halogenes) one can expect not only high hardness intrinsic in covalent nets of rigid bonds, but also metallic conductivity. These materials are highly desired for industry in order to replace the sintered powders of superhard (diamond, cBN) and conductive (Co) materials. Silicon compounds with clathrate [22, 23] and zeolite [23, 24] structure are archetypical and can serve as an existent point of departure.

Silicon clathrates with structures often isotypical to gas hydrates of types I (A_8Si_{46}) and II ($A_{24}Si_{136}$) [22] 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. So they are the hardest known clathrates with highest elastic moduli. In particular, the hardness, just like the bulk modulus and other elastic constants, is close to that of conventional diamond silicon Si-I, even in the case of empty-cage Si_{136}. The rigidity of silicon framework is defined by Si–Si bondings, and both intercalated metals and voids do not influence it much. The known silicon clathrates are thermoelectric and superconducting materials [19]. The compounds of alkali and alkaline earth metals can be obtained by thermal decomposition of Zintl type silicides (e.g., Na_4Si_4, Ba_2Si_4). However, the stoichiometric bulks of the best properties can be obtained only at the p, T-domain(s) of the thermodynamic stability of clathrates, i.e., at HPHT conditions [23], where such clathrates can be formed directly from the elements. However, the HPHT phase transformations in clathrate-forming systems have not been studied so far, although the study of Na–Si system under pressure attracts much attention due to the recent discovery of a high-pressure $NaSi_6$ clathrate [23] that allowed obtaining the orthorhombic allotrope of silicon with promising for optoelectronics quasidirect bandgap, Si_{24} [24]. Also, in order to design B- and C-bearing clathrates, understanding of mutual stability of the Na–Si compounds remains a challenging problem that has been partially solved in the present letter.

Here we experimentally studied the phase boundary between sodium clathrate materials (Na_8Si_{46}, type I and $Na_{24+x}Si_{136}$, a high-pressure form of type II with x up to 6.5) and their formation from Na+Si mixture and decomposition. The high-pressure sytheses and transformations of silicon clathrates up to 6 GPa and 1500 K were carried out using the standard Paris–Edinburgh cells (opposite-anvil geometry), previously well characterized during other in situ p, T-studies [6, 25]. The initial Na+Si mixture (commercial products, handled in Ar atmosphere) or clathrate II (HP synthesis, handled in air) were placed into cylindrical capsules from hexagonal boron nitride (volume ~3mm^3) and sealed with a BN cap. The capsules were placed within the graphite cylinders (furnaces) assuring the electro-resistive heating. Pyrophyllite or boron–epoxy gaskets were employed as a pressure trasmitting medium. Additional Teflon rings were placed around the gaskets to avoid the lost of cell pressure due to the material leakage (especially in

the case of pyrophyllite). Typical experiments were performed between 3 and 6 GPa at temperatures from 900 to 1500 K (heating time from 0.5 to 3 h) using standard 10/3.5 assembly (Fig. 1, *a*). Pressure calibration for a boron–epoxy gasket (pressure medium) has originally been performed in situ using 300 K equation of state (EOS) of hBN. It was confirmed in our experiments by EOS of Si and Na and can be presented as $p_{cell}(\text{GPa}) = 0.0125 \times p_{oil}(\text{bars}) - 8.85 \times 10^{-6} \times [p_{oil}(\text{bars})]^2$ (typical pressure reproductibility ±0.5 GPa). In the case of pyrophyllite gasket the cell pressure–oil pressure curve was the same within reproductibility (according to the EOS of Si). Temperature calibration (*T*-power curve) has been obtained using a number of *in house* experiments with K-type thermocouple (hBN sample). In situ observations of Si melting at the known pressure (see Fig. 1, *b*) allowed us to refine the calibration to T (K) = 300+3.25×power (W) (typical temperature reproductibility ±50 K). Similar values of power (±5 W) required for Si melting were observed in the case of both boron–epoxy and pyrophyllite gaskets.
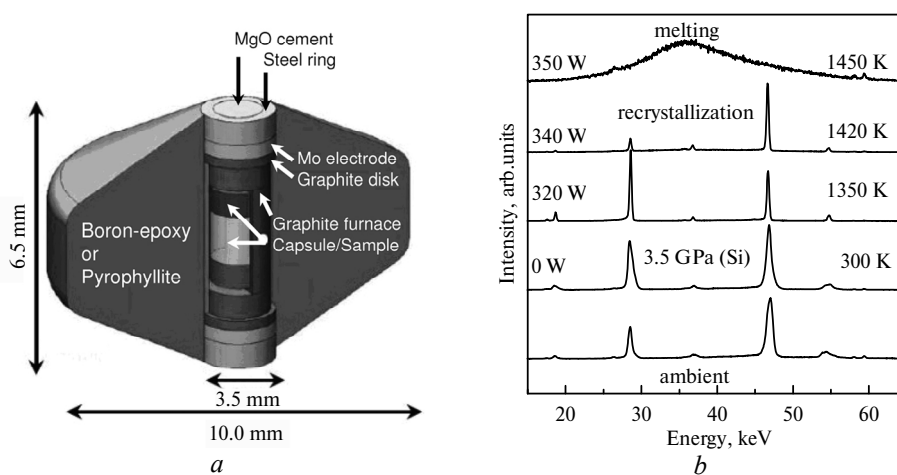

Fig. 1. (*a*) Drawing, materials and dimensions of standard 10/3.5 assembly of the high-pressure cell for opposite-anvil Paris–Edinburgh press. (*b*) In situ data (beamline PSICHE, synchrotron SOLEIL) on the power of Si melting at 3.5 GPa in boron–epoxy gasket (Si gauge [26]). 350 W corresponds to ~ 1450 K according to the melting curve of Si [27].

Our in situ experiments at PSICHÉ beamline of synchrotron SOLEIL have shown that silicon melts at power of ~ 350 W at 3.5 GPa (see Fig. 1, *b*), well in agreements with expected 1450 K according to thermocouple calibration curve and melting curve of silicon [27]. All transformations between clathrates (and reactions of Na or Na_4Si_4 with Si) typically occur below silicon melting curve.

In situ data on the synthesis (ESRF, ID 27) is presented in Fig. 2, *a*. At 4 GPa the mixture of Na+Si has been heated. First Na reacts with Si leading, probably, to disordered Na_4Si_4 with broad XRD reflections. At high temperatures the clathrate II crystallizes, while further temperature increase leads to the clathrate I formation. This sequence of transformations is well in agreement with ex situ experiments described in [28]. We should note that the duration of our experiments was of ~ 0.5–3 h, while in [28] the corresponding powders were obtained within 20 min, and single crystals during ~ 1 h. This fact is indicative of the temperature (and not time) impact on the relative stabilities of structures I and II: type II is stable at lower temperature, while type I at higher temperatures, at least at pressures of ~ 4–5 GPa.
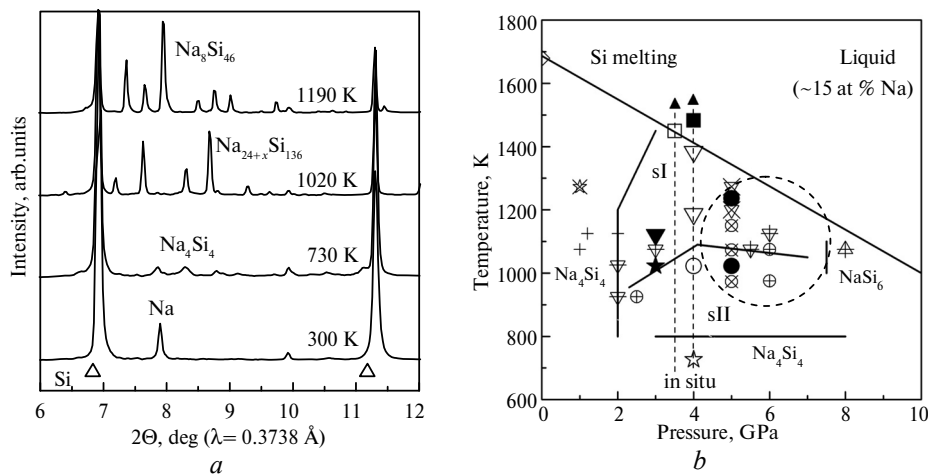
Fig. 2. (*a*) In situ XRD data on phase/chemical transformations in the Na+Si mixture (~ 15 at % of Na) during heating at 4 GPa obtained at ID27 (ESRF). (*b*) The clathrate transformation diagram in the Na–Si system. Most of the experimental points correspond to 15–20 at % of Na. Symbols represent compounds recovered or observed in situ (Na$_4$Si$_4$ is ★,☆, sI-Na$_8$Si$_{48}$ is ▼,▽, sII-Na$_{24+x}$Si$_{136}$ is ●, ○, NaSi$_6$ is ▲, △, and melt is ■, □). Solid symbols indicate the results of our recovery experiments, open symbols indicate our in situ data. For comparison, the ex situ data from other works are also shown: symbols crossed with + for data from Kurakevych et al. [23], and with × from Yamanaka et al. [28]. Solid lines are given to guide the eyes.

The transformation diagram based on the in situ (see Fig. 2, *a*) and ex situ (table) experiments is presented in Fig. 2, *b*. In general, our data is well in agreement with previous results of the synthesis of polycrystalline samples in Ta capsules by Kurakevych et al. [23], and of single crystal growth in boron nitride capsules by Yamanaka et al. [28]. The different time scales of experiments allow speaking about the closeness, at least in part, of this diagram to the isopleth section (~ 15 at % Na) of the *p*, *T*, *x*-phase diagram of the Na–Si system. However, strong non-stoichiometry of type II clathrate (in fact, the large cages, a characteristic feature of clathrate II, can host two atoms of sodium under pressure) seems to render the situation more complicated. The dashed circle in Fig. 2, *b* indicates the most questioned *p*, *T*-region at present time, where the competition of crystallizing phases is remarkable and very sensitive to the sodium concentration. At higher pressures, NaSi$_6$ clathrate becomes stable, at least at high temperatures and sodium concentrations close to the compound stoichiometry [23]. Below ~ 2 GPa, no clathrates can be formed in the system, instead, Zintl compound Na$_4$Si$_4$ seems to be the only stable compound [23] that can be also recovered [28].

Finally, a tentative diagram of the formation and stability of Na–Si clathrates has been proposed. At low pressures (below 2 GPa), no clathrate synthesis is possible. Between 3 and 6 GPa one can obtain Na$_4$Si$_4$, clathrate II and clathrate I with the temperature increase. Above 7 GPa the clathrates NaSi$_6$ become stable at high temperatures. The obtained results allow us to suggest that most probable candidates for boron- and carbon-bearing clathrates are doped type I compounds (e.g., Na$_8$C$_y$Si$_{46-y}$ or Na$_8$B$_x$Si$_{46-x}$ with *x* up to 8 corresponding to Zintl phase with highest hardness), since the stability temperature of clathrate I is the highest among other structural types and close to the onset of B and C atom's mobility in possible precursors that may be used as sources of boron and carbon (boron silicides, SiC, etc.).

Experimental details and phase composition of recovered samples (ex situ data)

No	Composition	Pressure	Temperature	Recovered phases			
				Si	clathrate		Na$_4$Si$_4$
					I	II	
Z004	Si + Na (15 at %)	5 GPa	1230 K	+		++	
Z007	HP clathrate II	3 GPa	1120 K	+	++		
Z008	(+ NaCl)	3 GPa	1020 K	+		+(?)	++
Z009		5 GPa	1020 K	+		++	+(?)
Z014	Si	4 GPa	1480 K	melt			

Вивчено in situ i ex situ процес утворення при високих тисках i стабільності клатратів Na$_8$Si$_{46}$ (структура I) i Na$_{24+x}$Si$_{136}$ (структура II). Експерименти було проведено в стандартних Париж-Единбурзький комірках (opposite anvils) при тисках i температурах до 6 ГПа i 1500 K відповідно. Встановлено, що хімічна взаємодія в системі Na–Si i переходи між двома структурами клатратів відбуваються при температурах нижче температури плавлення кремнію. Запропоновано перше наближення діаграми перетворень клатратів. Відзначено велику чутливість продуктів кристалізації до концентрації натрію. Na$_{24+x}$Si$_{136}$ (структура II) є стабільною при більш низьких температурах у порівнянні з Na$_8$Si$_{46}$ (структура I), принаймні до ~ 6 ГПа.

Ключові слова: клатрати кремнію, інтерметалічні сполуки, фазова діаграма, синтез.

Изучен in situ и ex situ процесс образования при высоких давлениях и стабильности клатратов Na$_8$Si$_{46}$ (структура I) и Na$_{24+x}$Si$_{136}$ (структура II). Эксперименты были проведены в стандартных Париж-Эдинбургских ячейках (opposite anvils) при давлениях и температурах до 6 ГПа и 1500 K соответственно. Установлено, что химическое взаимодействие в системе Na–Si и переходы между двумя структурами клатратов происходят при температурах ниже температуры плавления кремния. Предложено первое приближение диаграммы превращений клатратов. Отмечена большая чувствительность продуктов кристаллизации к концентрации натрия. Na$_{24+x}$Si$_{136}$ (структура II) является стабильной при более низких температурах по сравнению с Na$_8$Si$_{46}$ (структура I), по крайней мере до ~ 6 ГПа.

Ключевые слова: клатраты кремния, интерметаллические соединения, фазовая диаграмма, синтез.

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