Na-Si phase diagram at HPHT

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Abstract

To construct an experimental phase diagram of the Na-Si system, it is important to emphasize that the compounds participating in the equilibria, i.e., Na_4Si_4, Na_8Si_{46} (sI) are stoichiometric. At the same time, non-stoichiometric phase is possible for $Na_{30.5}Si_{136}$ (sII-HP). Na_xSi_{136} is non-stoichiometric compound, “ideal” stoichiometry at x = 24 (for clathrate we adopt the coefficients in chemical formula corresponding to unit cell composition); x superior to 24 up to 30.5 correspond to high-pressure phase denoted as HP-sII (Yamanaka *et al.*, 2014), while at ambient pressure of Ar or in vacuum sII with x from 0 to 24 forms (Cros & Pouchard, 2009, Kasper *et al.*, 1965).

sII-HP coexists with Si-I at low temperatures, while sI becomes more stable at higher temperatures in the case of excess Si. Excess Na makes sII-HP stable up to the melting temperature. Previous reports suggest that ΔV of melting be close to 0 (Courac *et al.*, 2019), thus with weak slope dT/dp of melting curve. Rapid quenching of a stoichiometric liquid results in the crystallization of sII-HP, indicating that the melting of this phase is congruent. Some experiments show the coexistence of sI and sII-HP with the absence of Si-I. Figure represents the tentative phase diagram at 5 GPa compatible with all available experimental observations.

At pressures above 8 GPa, channel clathrate structure of Na_xSi_{24}, only phases with stoichiometries x = 4 or x ~0 are known (Guerette et al., 2018, Kim et al., 2015, Kurakevych et al., 2013). Long keeping of Na_4Si_{24} leads to sodium escape from the lattice, and its hydrolysis on the surface with air humidity. Anyway, heating in vacuum remains a method of choice to produce best samples of Si_{24} (Kim et al., 2015).

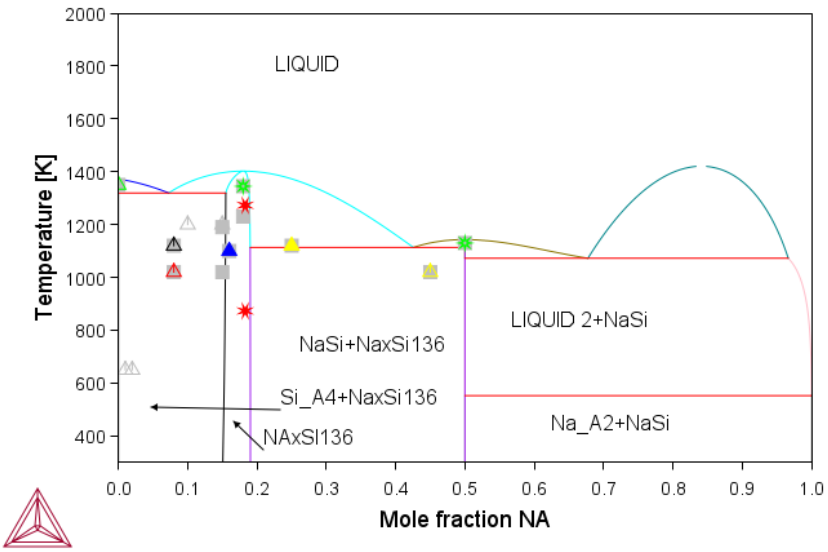

Figure. Phase diagram of Na-Si system at 5 GPa: experimental data vs CALPHAD simulation using ThermoCalc software.

References.

Courac, A., Le Godec, Y., Renero-Lecuna, C., Moutaabbid, H., Kumar, R., Coelho-Diogo, C., Gervais, C. & Portehault, D. (2019). *Inorganic Chemistry* **58**, 10822-10828.

Cros, C. & Pouchard, M. (2009). *Comptes Rendus Chimie* **12**, 1014-1056.

Guerette, M., Ward, M. D., Lokshin, K. A., Wong, A. T., Zhang, H. D., Stefanoski, S., Kurakevych, O., Le Godec, Y., Juhl, S. J., Alem, N., Fei, Y. W. & Strobel, T. A. (2018). *Crystal Growth & Design* **18**, 7410-7418.

Kasper, J. S., Hagenmul.P, Pouchard, M. & Cros, C. (1965). *Science* **150**, 1713-1714.

Kim, D. Y., Stefanoski, S., Kurakevych, O. O. & Strobel, T. A. (2015). *Nature Materials* **14**, 169-173.

Kurakevych, O. O., Strobel, T. A., Kim, D. Y., Muramatsu, T. & Struzhkin, V. V. (2013). *Crystal Growth & Design* **13**, 303-307.

Yamanaka, S., Komatsu, M., Tanaka, M., Sawa, H. & Inumaru, K. (2014). *J. Amer. Chem. Soc.* **136**, 7717-7725.