In-situ investigation of the thermal decomposition of clathrate-I \( \text{Ba}_{8-x}\text{Si}_{46} \) obtained by oxidation

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Since the discovery of the Ge(cF136) allotrope with emptied clathrate-II crystal structure [1], the oxidation of intermetallic phases at moderate temperatures has become a versatile route for the preparation of metastable clathrate phases, some of which have not been accessible so far by any other preparation method. By using gaseous HCl as oxidizing agent, the binary clathrate-I phases \( \text{Na}_{8-x}\text{Si}_{46} \) and \( \text{K}_{8-x}\text{Si}_{46} \), and the ternary clathrate-I phase \( \text{Na}_2\text{Ba}_6\text{Si}_{46} \) [2, 3] were prepared from the Zintl-phases \( \text{Na}_4\text{Si}_4 \), \( \text{K}_4\text{Si}_4 \) and \( \text{Na}_2\text{BaSi}_4 \), respectively. Recently, the oxidation of \( \text{Li}_2\text{Ba}_6\text{Si}_{46} \) and \( \text{Ba}_3\text{Si}_4 \) led to the clathrate-I phase \( \text{Ba}_{8-x}\text{Si}_{46} \) (\( x \approx 1.4 - 1.8 \)) [4]. This result is astonishing because this phase before had only been accessible by reacting mixtures of \( \text{BaSi}_2 \) and \( \text{Si} \) at high temperatures and at high pressures of several GPa [5]. The preparation of \( \text{Ba}_{8-x}\text{Si}_{46} \) at ambient pressure thus raises the question, whether \( \text{Ba}_{8-x}\text{Si}_{46} \) is actually a high-pressure phase. In all cases, the larger \( \text{Si}_{24} \)-cages centred by \( \text{Ba}_1 \) atoms at site 6\( d \) were found to be essentially fully occupied, and the smaller \( \text{Si}_{20} \)-cages centred by \( \text{Ba}_2 \) atoms at site 2\( a \) were partially occupied (Fig.1). Differently to the clathrate products from high pressure experiments showing high filling grades (\( \text{occ} (\text{Ba}1) > 0.75 \)), the clathrate products from oxidation showed distinctly low filling grades (\( \text{occ} (\text{Ba}1) < 0.4 \)) [4-7]. Essential insights on the stability of the clathrate-I phase at ambient pressure were already accessed by annealing experiments on products prepared at high-pressure [6, 7]. Herein, we report on the decomposition behaviour of a clathrate product from oxidation reaction.

![Fig. 1: Clathrate-I structure of \( \text{Ba}_{8-x}\text{Si}_{46} \). Large spheres represent \( \text{Ba} \) atoms in \( \text{Si}_{24} \)-cages (dark grey) and \( \text{Si}_{20} \)-cages (light grey).](image1)

![Fig. 2: X-ray powder patterns (\( \lambda = 0.53854 \text{ Å} \)) of a \( \text{Ba}_{8-x}\text{Si}_{46} \) sample recorded at various temperature steps.](image2)

A sample containing the clathrate phase at composition \( \text{Ba}_{6.20(1)}\text{Si}_{46} \) [4] was studied in the temperature range between 400 °C and 700 °C applying in-situ synchrotron X-ray powder diffraction. The experiment was carried out at the experimental station B2 of the HASYLAB laboratory, using a high-resolution powder diffractometer (Debye-Scherer geometry, on-site...
From room temperature to 500 °C, the crystal structure of the clathrate phase remained unchanged, apart from the expected thermal expansion (Fig. 3). The value for the linear expansion coefficient of $\alpha = 9.5 \times K^{-1}$ is in the expected range for silicon clathrates [8]. At 600 °C, the intensity ratio of the clathrate reflections changed markedly, caused by a distinct increase of the filling grade of Ba1. In the structure refinement, the occupancy factor increased from $occc(Ba1) < 0.1$ to $occc(Ba1) = 0.42(3)$. Simultaneously, the lattice parameter changed abruptly from $a(550 °C) = 10.3092(7) Å$ to $a = 10.3376(9) Å$. Remarkably, the refined clathrate composition of $Ba_{6.84(6)}Si_{46}$ at 600 °C is close to the composition of $Ba_{6.63}Si_{46}$ which was reported to form on annealing single crystals of the high pressure products at 527 °C [6]. However, the increase of Ba content observed here is only possible by partial decomposition of the clathrate phase and segregation of $\alpha$-Si. In fact, formation of $\alpha$-Si was also observed at 600 °C (Fig. 2). As the amount of $\alpha$-Si appears to be too large, we assume in addition crystallization of an amorphous Si by-product present in the starting material [4]. At 650 °C, the clathrate phase at composition $Ba_{6.8}Si_{46}$ had decomposed to $BaSi_2$ and $\alpha$-Si, which was similarly observed on annealing of a high-pressure product at 627°C [7].

The results show that annealing of both, clathrate phase with high Ba content and low Ba content results in a similar product between 500 °C – 600 °C. This may indicate a stability maximum of the clathrate phase $Ba_{6.x}Si_{46}$ at $x \approx 1.3$ in this temperature range at ambient pressure.

References


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Fig. 3: Development of occupancy factors of the Ba sites (top) and of the lattice parameter (bottom) with temperature starting from $Ba_{6.20(1)}Si_{46}$ [4].