Progress in understanding of cage compounds

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Successful application of the high-pressure technique for the synthesis of new materials led to the binary compounds Sr_8Si_{46} and $MgSi_5$. We have achieved significant developments in the redox preparation in ionic liquids and the electrochemical control of the chemical conversion. The new clathrate-I borosilicides ($M_8B_xSi_{46-x}$, M = K, Rb, Cs) are unique among the intermetallic clathrate phases due to their structural organization caused by extreme volume confinement, and their remarkable chemical inertness.

Alkaline-earth metals and silicon do not form cage compounds at ambient pressure. In the Ba-Si system, the Zintl-phase $BaSi_2$ and Si(cF8) coexist at thermal equilibrium. By high-pressure and redox preparation, however, the superconducting clathrate-I Ba_{8-x}Si₄₆ was obtained. For the lighter earth-alkali metals, no cage compounds have been identified by this method so far. The high-pressure preparation of Sr₈Si₄₆ succeeded although it was predicted to be instable by theoretical calculations. Sr₈Si₄₆ was obtained at 5 GPa in the temperatures range between 1273 to 1373 K [1]. The phase features a narrow stability range and does not form at higher or lower pressures. At ambient pressure conditions, the compound is metastable and decomposes at ≈ 800 K into Si and HT-SrSi₂. Chemical bonding analysis revealed the expected covalent interaction within the silicon network and additional multi-center bonds between Sr and Si atoms, which comes along with the general tendency of an increasing metallic character under high-pressure conditions (Fig. 1). Sr₈Si₄₆ is a BCS type II superconductor with a transition temperature of $T_c = 3.8(3)$ K.

For Mg atoms, a clathrate compound was not expected to form because the small Mg atoms do not fit the



Fig. 1: Si_{20} cage in Sr_8Si_{46} combined with the pELI-D distribution calculated for the states above E_F . Red isosurfaces visualize multi-atomic Sr-Si bonding. pELI-D values are shown for the (020) plane.



Fig. 2: a) $MgSi_5$ crystal structure with fourfold bonded Si atoms; b) columns of condensed Si_{15} -cages filled by Mg atoms along [100].

characteristic polyhedral cavities. The only equilibrium phase in the Mg-Si system at ambient pressure is Mg₂Si crystallizing in the CaF₂ type of structure. By applying high-pressure, high-temperature conditions, the cage compound MgSi₅ has been obtained at p = 5 and 10 GPa between T = 1173 K -1373 K [2]. In the crystal structure, the Si atoms form a fourfold-bonded framework with columns of empty Si₈ cages, and Si₁₅ cages filled by Mg atoms (Fig. 2). MgSi₅ was identified by electron diffraction tomography and the crystal structure parameters were refined from single-crystal X-ray diffraction data. Besides two-center bonds within the silicon framework, the structure is characterized by strong multi-center Mg-Si bonding within the large cages and lone-pair-like interactions in the empty Si₈ cages.

Redox preparation in ionic liquids (ILs) was originally applied to synthesize the allotrope Ge (*cF*136). In these early experiments, the IL was rather a reactant than a reaction medium. New ILs were identified to be suitable inert reaction media, to which benzophenone was added as an oxidizer [3]. By reacting Na₁₂Ge₁₇ at 70 °C and annealing the product at 350 °C, metastable clathrate-II Na_{24- δ}Ge₁₃₆ was obtained with α -Ge [4]. On a time scale of several weeks, the composition of the clathrate changes at room temperature under argon atmosphere and loss of sodium becomes evident.



Fig. 3: Borosilicide clathrates adapt to extreme size constraints. Reduction of the bond lengths (red) allows a larger dodecahedron volume (yellow). The size of the sodalite cage (gray) scales with the lattice parameter.

Further development of the preparation procedure was achieved by electrochemical redox reactions. By using Na₁₂Ge₁₇ as an anode and Al as a cathode, metastable Ge(*cF*136)) and Na_{24- δ}Ge₁₃₆ were prepared at 280 °C in a salt melt [5].

Borosilicide clathrates constitute an own branch of intermetallic clathrates with a unique structural feature: Boron atoms first substitute atoms at Wyckoff site 16i, but not at site 6c as it is observed in other clathrate-I phases. Different compositions of the clathrate borosilicide $K_{8-x}B_ySi_{46-y}$ were investigated to understand the complex structural order in this clathrate type [6]. As a general trend, the compositions within the homogeneity range follow the Zintl-rule with $n(K) \approx$ n(B). The unit cell volume shrinks distinctly with boron content, and consequently it was quite unexpected that new representatives Rb₈B₈Si₃₈ [7] and $Cs_8B_8Si_{38}$ [8] formed at p = 8 GPa and T = 1273 K. Crystal structure analysis revealed the remarkable flexibility of the clathrate-I framework to combine extreme size constraints with large filler atoms. Despite their sophisticated preparation, borosilicide clathrates feature a conspicuous inertness once they are formed, and may thus have the potential for material science.



Fig. 4: Perovskite-related atomic arrangement in the crystal structure of $Hf_2B_2Ir_5$. Cuboctahedrons (orange) are separated by Hf_2Ir_4 octahedrons (white).

The cage compound $Hf_2B_2Ir_5$ constitutes a new structure type related to Mo_2FeB_2 , which can be described as intermetallic perovskite derivative. Additional Hf-Ir bonds form within the cages similar to the transition metals clathrates. In the crystal structure, B_2 dumbbells center columns of cuboctahedral Hf_4Ir_8 units, which are separated by chains of Hf_2Ir_4 octahedrons along [001] (Fig. 4). The compound is a promising electrocatalyst for the oxygen electrode in the water cleavage reaction (https://www1.cpfs.mpg.de:2443/CMS_01).

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