Intermetallic cage compounds

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Understanding cage compounds implies thorough analysis of the interrelations between crystal structure and physical behaviour, which is a key competence shared by the department of Chemical Metals Science. The main focus of our investigations are intermetallic clathrates offering tunable transport properties by changeable compositions. As a result of comprehensive studies we have achieved deeper insights into their defect chemistry theoretically and experimentally, and we continue preparing compounds which had been considered unattainable for decades. Herein, we report on distortions of the clathrate I framework in the system Ba-Au-Ge which result in different structural modifications. We introduce an unusual metastable clathrate I phase in the system Ba-Li-Si, where Li atoms show an ambivalent character by acting as cage atoms as well as framework atoms in the same crystal structure. Finally, we report the successful bulk preparation of the first type II clathrates containing Li atoms in the covalently bonded framework.

Clathrate I phases in the system Ba, Au, Ge

Today's publications on intermetallic clathrates have their origin largely in materials research and in the search for new thermoelectric materials. For the most frequent kind, type I phases with anionic framework and cationic filler atoms, the crystal structure with space group *Pm*-3*n* is considered well-known. However, our latest study on clathrate I phases in the system Ba-Au-Ge [1, 2] revealed an unexpected phase diagram mapping a wide composition range and complex phase relations between clathrate I modifications with different space groups (Fig. 1). In the clathrate structure, Au atoms and especially atom vacancies □ have a strong impact and cause local distortions of the covalent framework. In order to minimize the disturbance of the periodic order, vacancies at low concentrations tend to a homogeneous distribution with large mutual distances, while for high vacancy concentrations their ordered arrangement is more favourable. For the binary high temperature phase $Ba_8Ge_{43}\square_3$, vacancy ordering leads to a loss of symmetry elements and a 2 × 2 × 2 supercell with space group *Ia*-3*d* [3]. Since each vacancy is surrounded by 4 three bonded Ge anions, the electronic balance $(Ba^{2+})_8(3b\ Ge^-)_{12}(4b\ Ge^0)_{39} \times 4e^-$ implies four excess electrons and metallic behaviour. For the whole homogeneity range, the composition of the clathrate I phases can be described with good approximation by the formula $Ba_8Au_x\square_{3-0.563x}Ge_{43-0.437x}$. This means that by adding the Au atoms to the framework, excess electrons and vacancies are reduced likewise, till the semiconductor composition $Ba_8Au_{5.33}Ge_{40.67}$ is reached, which is described by the electronic balance $(Ba^{2+})_8(Au^{3-})_{5.33}(Ge^0)_{40.47}$. At 800°C, the superstructure of the high temperature phase $Ba_8Ge_{43}\square_3$ with space group *Ia*-3*d* is preserved for low Au content $0 \leq x \leq 1.1$. Within the composition range, investigations of rapidly quenched samples by HRTEM showed nanoscale fluctuations of composition, while the superstructure symmetry is evident only in varying degree (see report Ramlau). Following a two phase region, the crystal structure of the clathrate I phase at $x \geq 1.6$ surprisingly changes to a new tetragonal clathrate I variant with space group $P4_2/mmc$. The tetragonal structure results from vacancy ordering, which can be shown by drawing the clathrate I structure as a packing of 24 atom polyhedrons forming infinite columns along [100], [010] and [001] (Fig. 2). In the tetragonal structure, columns along [001] contain more vacancies

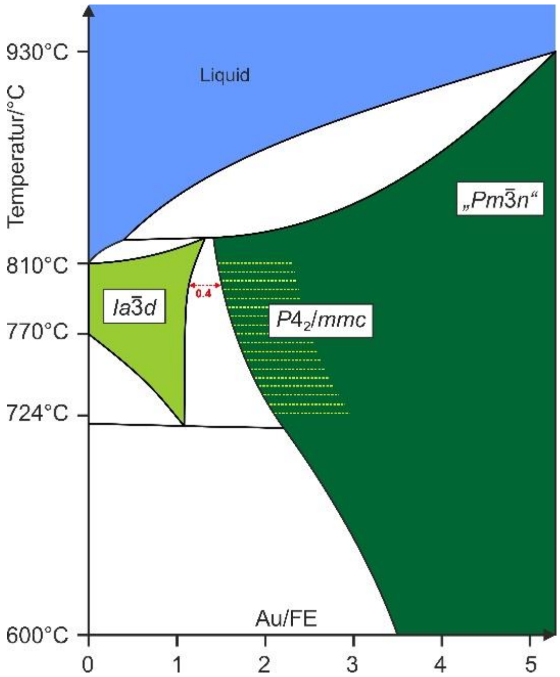

Fig.-1: Detail from the Ba-Au-Ge phase diagram along the concentration line $Ba_8Au_x\square_{3-0.563x}Ge_{43-0.437x}$.

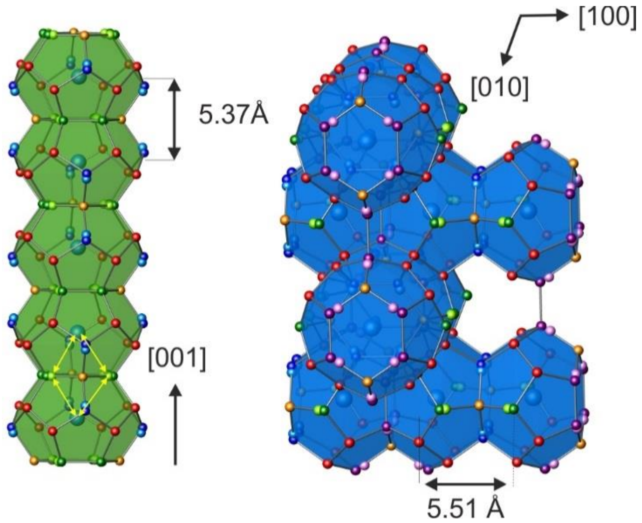

Fig.-2: Columns of 24 atom polyhedrons in the clathrate I structure with different number of vacancies along [100] and [001] directions.

than the perpendicular ones leading to a contraction by the bonding interaction of 3b Ge^- anions and Ba^{2+} cations. This is a typical case where the tetragonal symmetry can be masked by a pronounced Drilling formation.

With further increase of Au and decrease of vacancy content, the crystal structure approaches cubic symmetry of the direct super group *Pm*-3*n*. At composition $Ba_8Au_{5.33}Ge_{40.67}$, the phase is a *p*-type semiconductor and shows the best thermoelectric performance among the rarely observed *p*-type clathrates so far (*ZT* = 0.9 at 400 °C for bulk material) [4]. This result and the favourably low heat conductivity was not expected from the commonly accepted rattling model of heat conduction, where independent rattler modes of the filler atoms inside the cages scatter heat carrying acoustic phonons. From a chemical point of view it was hardly conceivable that negatively charged substitution atoms or vacancies allow for a decoupling of the heavy Ba atoms from acoustic phonons. This was further confirmed by bonding analysis applying ELI, which revealed covalent interactions between the negatively charged Au atoms and the Ba atoms in the cages [4]. In order to investigate the mechanism of heat conduction, neutron spectroscopy experiments were performed on a high quality single crystal. In fact, the phonon life time derived was rather long, ruling out the idea of an efficient phonon scattering by cage atoms. The reason for the low heat conductivity was found in the low energy of optical modes limiting the energy window for the heat carrying acoustic modes below [5]. The importance of this finding lies in the new direction to search for thermoelectric clathrate phases. Instead of small cations being independent rattlers in oversized cages, one might rather look for heavier cage atoms contributing to the soft acoustic modes by directed bonding to the framework.

Theoretical verification of vacancy stability

The experimental proof of atom vacancies in the clathrate framework is a field of extensive experimental studies. Theoretical modeling of such disordered systems is arduous as well and a definition of a simplified superstructure model is arbitrary. By applying elaborate density functional theory calculations with an all-electron full-potential electronic-structure code (FHI-aims), we could verify the defect arrangement of experimental structure analysis without imposing any biasing preconditions [6]. By considering configuration entropies and vibrational free energies, the thermodynamic stability of defect clathrates was correctly predicted. The calculation confirmed the contrasting behaviour of Si and Ge clathrates, where only the latter are stabilized by vacancies. Exemplarily, Fig. 3 shows the results for the clathrate I in the binary Ba-Ge system. The experimental finding of tree vacancies per formula unit was confirmed, which is preferred to the hypothetical ideal Zintl-phase $Ba_8Ge_{42}\square_4$. Moreover, the calculations confirmed that $Ba_8Ge_{43}\square_3$ is a high temperature phase formed by reaction of Ba_6Ge_{25} and α-Ge.

The ambivalence of Li atoms in clathrate I silicides

The chemistry of silicon clathrates might still be largely unknown. The reason is that silicon compounds show sluggish formation kinetics already at moderate reaction temperatures of 500 °C, while sufficiently

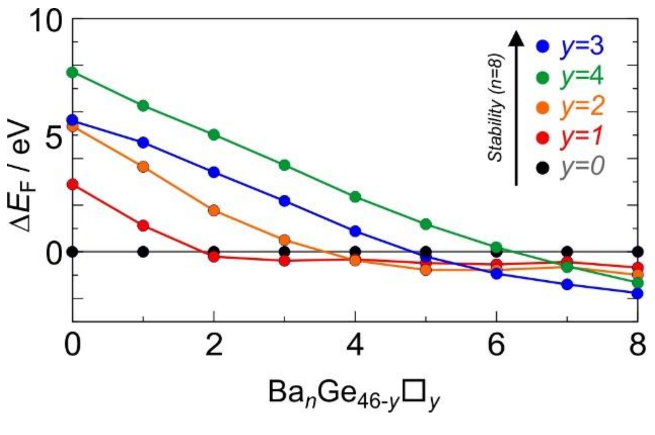

Fig.-3: Calculated energy of a binary clathrate model $Ba_nGe_{46-y}\square_y$ depending on Ba atoms in the cages and vacancy concentration in the framework.

high temperatures for solid state reactions exceed the stability limit of low temperature or metastable phases. A possible way out of this dilemma is the use of metastable precursor phases, which often show a high reactivity. Metastable precursor phases have been obtained by redox reactions (see report Böhme) or by quenching high pressure phases to ambient conditions. Following this concept, a mixture of the metastable clathrate I $Ba_{8-x}Si_{46}$ and the Zintl-phase $Li_2Ba_4Si_6$ was annealed at 400 °C in order to incorporate Li atoms into the clathrate. Although the incorporation of Li atoms was successfully achieved as anticipated, the formation of a non-classical clathrate I phase came unexpectedly: The phase $[Li_xBa_{8-x}][Li_ySi_{46-y}]$ shows the peculiarity that Li atoms are present in both cages *and* framework [7]. The presence of Li atoms in the clathrate was proven by combining X-ray powder diffraction, ^{7}Li and ^{29}Si solid state NMR analyses. Rietveld refinement revealed a reduced Si occupancy factor at site 2*a* of Ba and the framework site 6*c*. However, atom vacancies at 6*c* would contradict the interatomic distances to the surrounding atoms at 24*k*, which are larger than those of the binary phase $Ba_{6.80(3)}Si_{46}$. Subsequently, ^{7}Li NMR investigations not only confirmed the presence of Li atoms in the clathrate framework, but also the presence of two kinds of Li species (Fig. 4). From the calculated electronic density of Li(2*s*) states at Fermi level, the signal with distinct Knight shift was assigned to Li atoms of site 2*a* in the 20-atom cage. The composition $[Li_{0.59(2)}Ba_{7.41(2)}][Si_{43.7(1)}Li_{2.3(1)}]$ was obtained by assigning the deficient sites of the binary refinement model $Ba_{8-n}Si_{46-n}$ to Li atoms. Compared to the binary phase $Ba_{7.48(2)}Si_{46}$, the Knight shifts of the ^{29}Si NMR signals strongly decrease in the ternary phase pointing to a lower number of conduction electrons (Fig. 4). This can be understood when $[LiSi_4]^{3-}$ units are considered as filled silicon atom vacancies, which act as electron acceptors in the framework. However, a sufficiently high substitution of Si atoms to obtain an electron balanced semiconductor has not been achieved yet. As expected, the transition temperature T_c to the superconducting state is decreased by the substitution from 7.1 K for the binary clathrate to 3.2 K for the ternary one, which was similarly observed for the isoelectronically substituted clathrates $Ba_8Ag_xSi_{46-x}$.

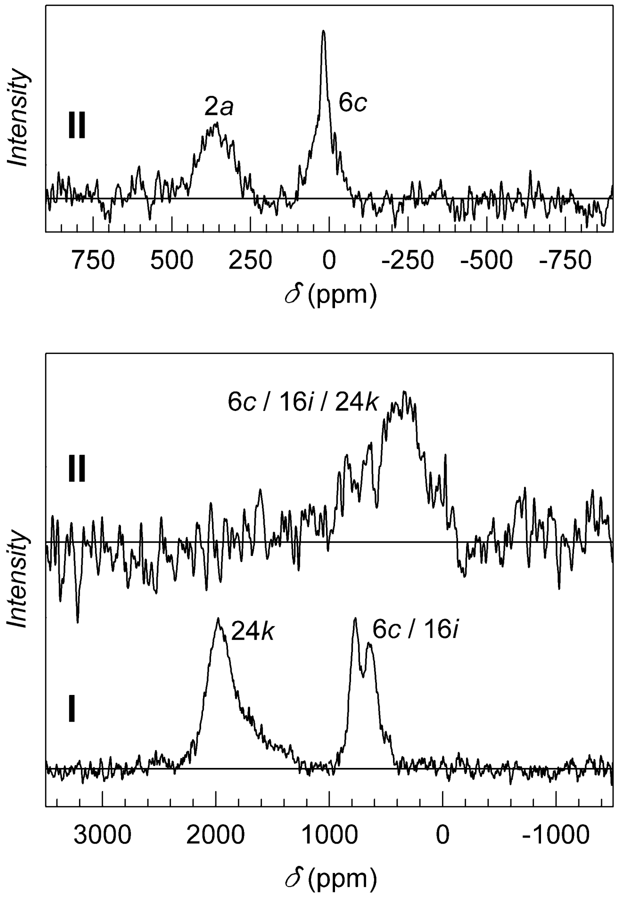

Fig.-4: Solid-state ^{7}Li (top diagram) and ^{29}Si (bottom diagram) NMR spectra recorded with echo techniques on static samples for $Ba_{7.48(2)}Si_{46}$ (I) and for $[Li_{0.59(2)}Ba_{7.41(2)}][Si_{43.7(1)}Li_{2.3(1)}]$ (II). The signals are labeled with the Wyckoff symbol of the assigned atomic site in the clathrate I crystal structure.

A clathrate II with Li-Ge framework

Compared with the more frequent clathrate I type, clathrate II phases with the general composition $M_{24-x}Y_{136}$ have yet been less investigated. The variation of physical properties by atomic substitution has been achieved only to a limited extent, while atom vacancies have not been detected so far. Typically, filled clathrate II phases show metallic behaviour and only exceptional cases like Si_{136} or Ge_{136} are semiconductors [8]. Inspired by finding the electron acceptors $[LiSi_4]^{3-}$ and $[LiGe_4]^{3-}$ in type I clathrates [7,9], we have investigated whether electron compensation in clathrate II phases can be achieved in this way. By annealing at 650°C, we have recently obtained the first clathrate II phase with a Li-Ge framework [10]. In this phase, which was obtained with the composition $Na_{16}Cs_8Li_xGe_{136-x}$ (x = 2.8), the $[LiGe_3]^{3-}$ acceptors only partly compensate the valence electrons of Na and Cs atoms according to the formal charge balance $[Na^{+}]_{16}[Cs^{+}]_8[LiGe_4{}^{3-}]_{2.8}[Ge^{0}]_{122} \times 15.6\ e^{-}$ (Fig. 5).

The presence of excess electrons is in agreement with the large Knight shift of ^{23}Na and ^{133}Cs NMR signals. As observed in Li substituted clathrate I phases [9], the Knight shift of more ionic Li atoms in the framework

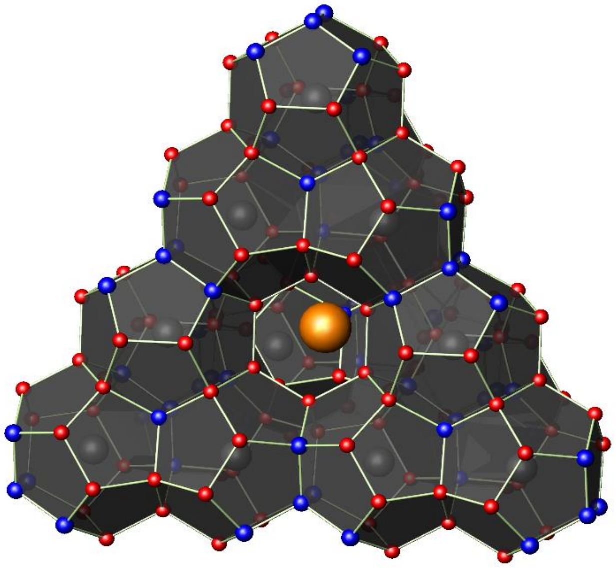

Fig.-5: Clathrate II structure of $Na_{16}Cs_8Li_{2.8}Ge_{133.2}$. Na atoms are drawn grey, Cs atoms orange, the framework sites partly occupied by Li atoms red.

is less pronounced. The crystal structure refinement from X-ray powder data reveals that among the framework sites 8*a*, 32*e* and 96*g* only the latter is occupied by Li atoms. This is plausible as substitution at this site is supported by a flexible atomic environment and causes less distortion of the long range order. Considering the high stability of the closely related $Na_{16}Cs_8Ge_{136}$, which congruently forms from the melt, the Li substitution is remarkable. It points to a high stability of $[LiGe_3]^{3-}$ acceptors in the framework, opening a new perspective to obtain electron compensated and thus semiconducting clathrate II phases in this way. This aspect is of high interest for materials science.

External Cooperation Partners

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