A new preparation route to intermetallic clathrates

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Clathrate compounds based on Group 14 elements and electropositive metals are expected to be promising thermoelectric materials[1]. The high expectations to this class of materials arise from their typically low thermal conductivity, which is an intrinsic property of the crystal structure. On the other hand, the charge carrier concentration in clathrate compounds can be influenced by an appropriate choice of the chemical composition. Usually, intermetallic clathrates are semiconductors or bad metals. Although the thermoelectric properties at ambient conditions are not competitive yet, it is expected that intermetallic clathrates have a potential for applications at elevated temperatures.

Most frequently, clathrates of type-I crystal structure are obtained, which has an ideal composition of M_8E_{46} and consists of two kinds of polyhedra, the dodecahedra E_{20} $[5^{12}]$ and the tetrakaidecahedra E_{24} $[5^{12}6^2]$ (Fig.1).
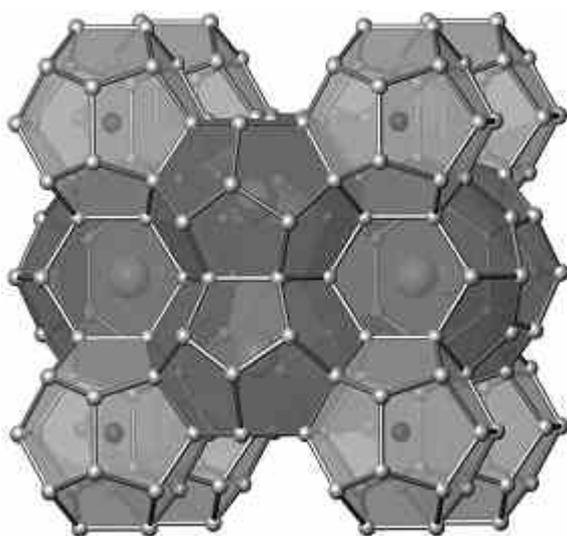

Fig.1: Crystal structure of type-I clathrates with E_{20} polyhedra (light grey) and E_{24} polyhedra (dark grey)

The four-bonded clathrate-I host framework E_{46} can be entirely formed with the valence electrons of group 14 elements E. The valence electrons donated by the guest metal atoms M are not required for the formation of the covalent bonds of the E_{46} framework. In the case of binary silicon clathrates, these electrons occupy antibonding states. Therefore, compounds like $K_{8-x}Si_{46}$ are metals[2] and expected to show a lower thermoelectric performance.

Semiconducting clathrates can be obtained by partial substitution of the group 14 atoms by trivalent group 13 atoms resulting in compounds like $K_8Ga_8Si_{38}$ [3] or $Ba_8Ga_{16}Ge_{30}$ [4]. With the electronic balances $[K^+]_8[Ga^-]_8[Si^0]_{38}$ and $[Ba^{2+}]_8[Ga^-]_{16}[Ge^0]_{30}$ these compounds follow the (8-N) rule and the Zintl-Klemm concept[5].

Differently from the silicon based compounds, clathrates of the heavier group 14 homologues Ge and Sn may contain voids $\square$ on the framework positions. In this case, the valence electrons of the guest metal atoms are formally transferred to three bonded anions (3b) Ge^- or (3b) Sn^-, surrounding the voids. In the compound $K_8Ge_{44}\square_2$, for example, two defects and eight (3b) Ge anions per unit cell are formed, corresponding to the valence electrons of 8 K atoms[6]. Thus, the charge balance can be considered as $[K^+]_8(3b)[Ge^-]_8(4b)[Ge^0]_{36}$.

The formation of defects is also known for other binary type-I clathrates such as $K_8Sn_{44}\square_2$ [7], $Rb_8Sn_{44}\square_2$ [8] and $Cs_8Sn_{44}\square_2$ [9]. Defects, substitution atoms, and the occupation of antibonding states can also occur together in the same compound. This is demonstrated for the first clathrates with group 9 elements $Ba_8CoGe_{43-x}\square_{2+x}$ (*Pm-3n*, $a = 10.670(1)$ Å), $Ba_8RhGe_{43-x}\square_{2+x}$ (*Pm-3n*, $a = 10.688(1) - 10.698(1)$ Å) or $Ba_8Rh_2Si_{44}$

(Pm-$3n$, a = 10.347(1) Å). The transition metal atoms in these compounds substitute framework positions.

The introduction of a void into the E_{46} framework causes locally a considerable distortion of the crystal structure and a displacement of the neighboring atoms. In the averaged view on the crystal structure by X-ray diffraction, the occupancy of the void position is found to be lowered. In addition, the voids are indicated by split positions of the surrounding atoms (Fig. 2).
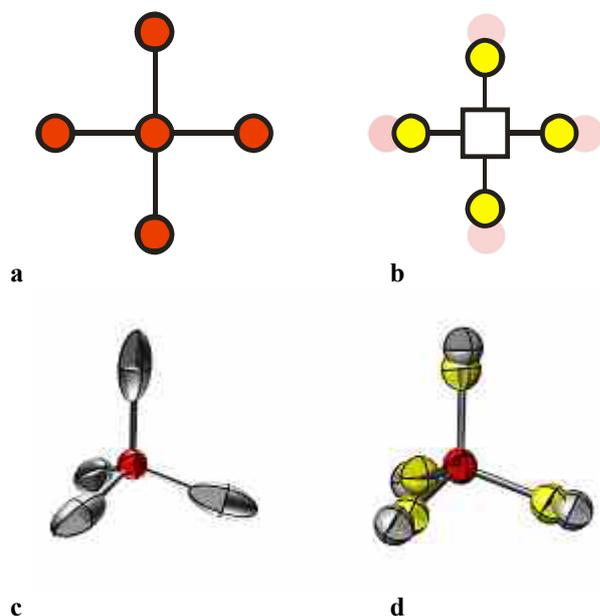

a   **b**

c   **d**

Fig.2: Defects in the clathrate framework cause local distortions resulting in split positions.

The ordering of the valence defects can result in the formation of superstructures, which were described from extended single crystal analyses with a 2 × 2 × 2 super cell (Pm-$3n$ → Ia-$3d$)[10-12].

We observed the formation of several kinds of super cells for all known defect clathrates, depending on the reaction conditions. Strictly speaking, the extend of ordering, the space group, the lattice parameters as well as the physical properties of defect clathrates depend on the system and the exact synthesis conditions.

As another possibility for the variation of the physical properties of clathrates, the chemical composition can be changed by removing guest metal atoms from the cages. This was rather possible so far, when the charge of the cage metal atoms is balanced by occupied antibonding states as in the binary alkali metal silicides. This was demonstrated with the synthesis of Si(cF136), by thermal decomposition of Na$_x$Si$_{136}$[13]. However, the removal of guest metal atoms from the cages was not achieved, when the valence electrons of the guest metal atoms are balanced by defects or group 13 atoms.

A new low-temperature method for the preparation of clathrates is the oxidation of precursor compounds by acidic protons. Ge(cF136) was synthesized this way by the oxidation of Na$_{12}$Ge$_{17}$ at 300°C in an ionic liquid of DTAC/AlCl$_3$ under argon atmosphere[14]. The acidic protons are delivered by the β-H-acidic DTAC, which undergoes a Hofmann elimination under reaction conditions.
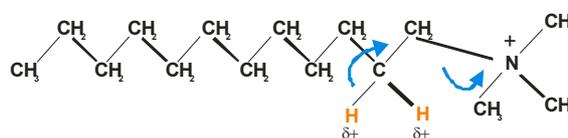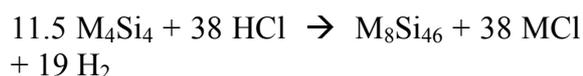

Fig. 3: Hofmann elimination of n-dodecyl-trimethylammonium chloride (DTAC)

The understanding of the heterogeneous character of the oxidation led to a further development of the synthesis method and the controlled oxidation of precursor compounds with gaseous HCl [15].

11.5 M$_4$Si$_4$ + 38 HCl → M$_8$Si$_{46}$ + 38 MCl + 19 H$_2$

The preparation route depends in detail on the choice of the HCl source. For a simplified reaction setup, gaseous HCl can be produced by dissociation of NH$_4$Cl into HCl and NH$_3$. For the synthesis it is important to place the precursor compound and NH$_4$Cl in different vessels at the

beginning of the reaction (Fig.4). Otherwise, amorphous compounds are formed from reactions, happening at lower temperatures at the beginning of the heat treatment.
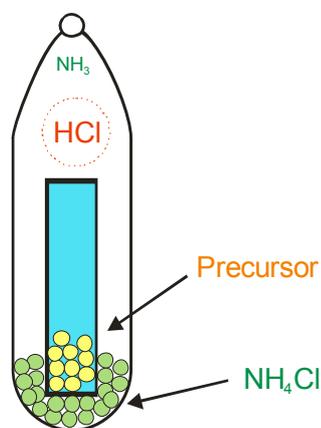

Fig. 4: Simplified experimental setup for the oxidation of precursor compounds with gaseous HCl.

This way, the type-I clathrates $Na_{6.2}Si_{46}$ (*Pm-3n*, $a = 10.199(1)$ Å) and K_7Si_{46} (*Pm-3n*, $a = 10.278(1)$ Å), have been obtained with a distinctly lowered occupancy of cage atom positions[15]. The synthesis method could be extended to clathrates containing alkaline earth metals like $Na_2Ba_6Si_{46}$ (*Pm-3n*, $a = 10.281(1)$ Å)[16] and Ba_6Si_{46} (*Pm-3n*, $a = 10.274(1)$ Å). The synthesis of Ba_6Si_{46} is especially remarkable, because Ba/Si clathrates were only known from high pressure syntheses[17].

Further optimization of the synthesis conditions in the Na / Si system led to a considerable reduction of the sodium content, which was determined by Rietveld refinement. The lattice parameters were refined from reflection positions determined by single profile fit. LaB_6 was used as internal standard (Tab. 1).
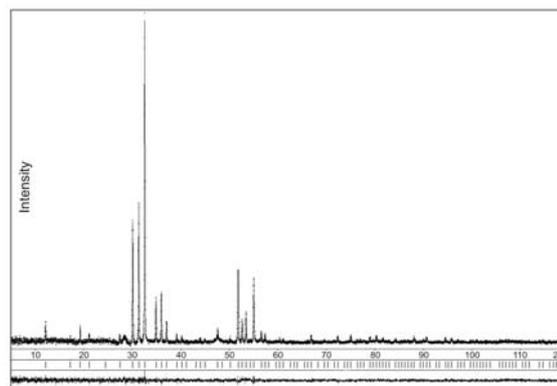

Fig. 5: X-ray powder pattern of K_7Si_{46} obtained from oxidation of K_4Si_4 with gaseous HCl. KCl was removed with water.

Tab. 1: Type-I clathrates obtained from thermal decomposition reactions

Refined composition	a / Å
$Na_{6.2}Si_{46}$	10.199(1)
$Na_{4.5}Si_{46}$	10.200(1)
$Na_{3.9}Si_{46}$	10.193(1)
$Na_{1.7}Si_{46}$	10.175(1)

The results show that it is conceivable to prepare a new silicon modification Si(*cP*46) with empty clathrate-I structure by the oxidation method. The optimization of the synthesis conditions is currently under investigation.

The oxidation method provides a general preparation route which is scalable and allows the synthesis of large amounts of products with standard laboratory equipment. Usually, fine powders are obtained and, therefore, the thermoelectric properties of the products have not been determined yet. Currently the densification of the reaction products is under investigation.

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