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Synthesis of the Clathrate-II $K_{8.6(4)}Ge_{136}$ by Oxidation of K_4Ge_9 in an Ionic Liquid

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The new clathrate-II $K_{8.6(4)}Ge_{136}$ has been synthesized by mild oxidation of K_4Ge_9 in the ionic liquid *n*-dodecyltrimethylammonium chloride (DTAC)/$AlCl_3$ at 300 °C and subsequent annealing at 370 °C. Refinement of the crystal structure from X-ray powder diffraction data revealed the composition $K_{8.6(4)}Ge_{136}$ [space group $Fd\bar{3}m$, $a = 15.302(1)$ Å], which was also confirmed by energy-dispersive X-ray spectrometry (EDXS), transmission electron microscopy, and scanning electron microscopy on the bulk material. K atoms preferably occupy the larger Ge_{28} cages rather than the Ge_{20} cages in the clathrate-II structure. $K_{8.6(4)}Ge_{136}$ is metastable and was found to decompose exothermically at 471 °C.

Introduction

The motivation for preparing new clathrates based on group 14 (Si, Ge, and Sn) elements comes from the desire to explore their remarkable crystal chemistry and unusual combination of physical properties.[1] Type-II clathrates, analogous with the gas hydrate $G_{24}(H_2O)_{136}$ (G = H_2S, CO_2, CCl_4)[2] and the clathrasil dodecasil-3C,[3] feature a cage network of four-bonded atoms composed of face-condensed 20-vertex pentagonal dodecahedra and 28-vertex hexakaidecahedra. Despite many extensive studies on intermetallic clathrates over decades, the synthesis of type-II clathrates remains a challenge. Thermal decomposition of the monosilicides and monogermanides to M_xSi_{136} and M_xGe_{136} has only been successful with Na (with Si and Ge) and Cs (with Si).[4] Direct reaction of the elements by using differently sized metal atoms was demonstrated by the preparation of $A_8Na_{16}Si_{136}$ and $A_8Na_{16}Ge_{136}$ (A = Cs, Rb).[5] The controlled removal of Na atoms from $Cs_8Na_{16}Ge_{136}$ was then used to prepare Cs_8Ge_{136}.[6] Similarly, Si($cF136$) was obtained from Na_xSi_{136}.[7] However, the use of this approach or the direct reactions of the elements have not resulted in any potassium-based clathrate-II, neither with Si nor with Ge, and this observation can be attributed to thermodynamic reasons. Therefore, low-temperature synthesis was considered, in order to access metastable compounds. The general synthetic approach of an oxidative polymerization and reorganization of cluster anions in polar intermetallic precursor phases has become increasingly more important. Controlled oxidation reactions are conveniently performed in solution; e.g., Ge_9^{4-} cluster anions dissolved in ethylenediamine were polymerized to linear polymers of vertex-linked clusters,[8] and, by using surfactants, the oxidative polymerization was directed to form mesoporous Ge.[9] Similarly, nanoporous forms of Si and Ge result from the heterogeneous oxidation of reactive precursors,[10] and $K_8Hg_{3+x}Ge_{43-x}$ was obtained by reaction of K_4Ge_9 with HgO.[11]

A promising synthesis route to crystalline clathrate compounds is the controlled oxidation of reactive precursor phases with acidic protons. The new Ge allotrope, Ge($cF136$),[12] with an empty clathrate-II crystal structure, was obtained from the mild oxidation of $Na_{12}Ge_{17}$[13] in an ionic liquid (IL) formed from *n*-dodecyltrimethylammonium chloride (DTAC) and $AlCl_3$. The clathrate-I silicides $Na_{6.2}Si_{46}$, $K_{7.0}Si_{46}$, and $Na_2Ba_6Si_{46}$ can be obtained by oxidation of Na_4Si_4, K_4Si_4, and Na_2BaSi_4, respectively, with gaseous HCl.[14] The title compound, $K_{8.6(4)}Ge_{136}$, was synthesized by mild oxidation of K_4Ge_9[15] in the IL (DTAC/$AlCl_3$) at 300 °C, followed by further annealing.

Results and Discussion

The oxidation of K_4Ge_9 to $K_{8.6(4)}Ge_{136}$ resembles the method recently applied for the synthesis of Ge($cF136$).[12] However, the Ge allotrope was obtained directly by the mild oxidation of $Na_{12}Ge_{17}$[13] in an IL, while the reaction of K_4Ge_9 under the same conditions led to an X-ray

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amorphous product. Crystalline samples of the clathrate-II $K_{8.6(4)}Ge_{136}$ were only obtained after further annealing of the crude product. In the first step, K_4Ge_9 was placed in glass vessels containing an IL (1:1 molar ratio of DTAC/$AlCl_3$). The reaction mixture was jacketed in a closed glass tube and heated for 1 day at 300 °C. The resulting product was washed with acetone and water, and vacuum dried. X-ray powder diffraction patterns of the intermediate product indicate a poorly crystalline material with broad reflections consistent with a clathrate-II type structure. Energy-dispersive X-ray spectrometry (EDXS) of the intermediate product by scanning electron microscopy (SEM) indicates a K/Ge atomic ratio of 8(1):92(1) compatible with a composition "$K_{12}Ge_{136}$". High-resolution transmission electron microscopy (HRTEM) investigations on the X-ray amorphous crude product are currently in progress. The crude product was then annealed under static vacuum at 370 °C for 2 days and transformed to polycrystalline $K_{8.6(4)}Ge_{136}$ (Figure 1). Annealing at slightly different temperatures leads to amorphous products and α-Ge.

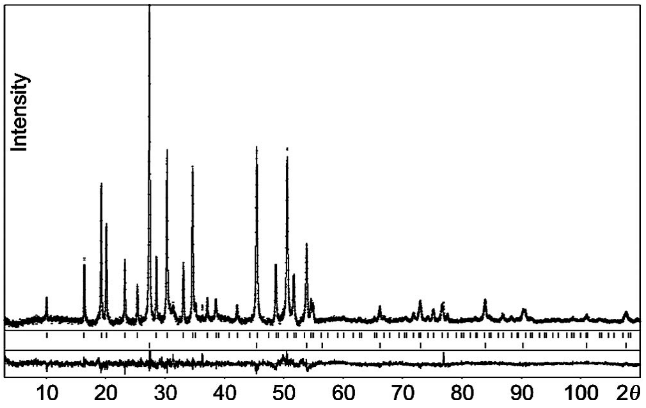

Figure 1. X-ray powder diffraction pattern of $K_{8.6(4)}Ge_{136}$ (Cu-$K\alpha_1$ radiation): experimental data (points), calculated profiles (line, top), reflection positions of $K_{8.6(4)}Ge_{136}$ (ticks, top line) and α-Ge (ticks, bottom line), as well as the difference curve (bottom).

Crystalline α-Ge was found as a minor phase (ca. 4 mass-%) based on the result of X-ray powder diffraction (XRPD) analysis. Chemical analysis of the annealed product using EDXS/SEM revealed a bulk composition of 5 at.-% K and 95 at.-% Ge, consistent with the results of the crystal structure refinement. Results of the refinement and crystallographic information are summarized in Table 1. The lattice parameter of $K_{8.6(4)}Ge_{136}$ [a = 15.302(1) Å] is distinctly larger than that of the empty clathrate-II Ge (cF136) [a = 15.212(1) Å],[12] smaller than that of Na_xGe_{136} (a = 15.4 Å)[4b] and $Cs_8Na_{16}Ge_{136}$ [a = 15.480(1) Å],[5] and similar to that of Cs_8Ge_{136} (a = 15.329 Å).[6] The crystal structure of clathrate-II is hierarchically related to $MgCu_2$,[16] and its unit cell contains 16 Ge_{20} and 8 Ge_{28} cages with 24 positions available for the guest atoms. The large germanium cages are condensed via their common hexagonal faces to form a diamond-like arrangement of four-connected polyhedra (Figure 2). The structure refinement yields an almost complete K occupancy within the Ge_{28} polyhedra [SOF = 0.89(2)], and a low occupancy within the smaller Ge_{20} cages [SOF = 0.09(2)]. The observed Ge–Ge distances in $K_{8.6(4)}Ge_{136}$ are 2.428(1), 2.462(1), 2.465(1), and 2.497(1) Å. The average Ge–Ge distance of 2.463(1) Å is larger than 2.453 Å for Ge(cF136)[12] and smaller than 2.494 Å[5] for the completely filled $Cs_8Na_{16}Ge_{136}$. This is consistent with a rigid band model that assumes valence electrons from the guest atoms occupy Ge–Ge antibonding states. This is confirmed by band structure calculations on an idealized K_8Ge_{136} model. The calculated density of states (DOS) also indicates that K_8Ge_{136} is a poor metal. Details of the calculations on $K_{8.6(4)}Ge_{136}$ are presented in the Supporting Information.

Table 1. Crystallographic data for $K_{8.6(4)}Ge_{136}$ [space group $Fd\bar{3}m$, origin choice 2, a = 15.302(1) Å].

Atom	Site	x	y	z	Occupancy	B_{iso} /Å^2
K1	8b	3/8	3/8	3/8	0.89(2)	3.1(6)
K2	16c	0	0	0	0.09(2)	2.0(38)
Ge1	8a	1/8	1/8	1/8	1	0.7(3)
Ge2	32e	0.2166(2)	x	x	1	1.7(2)
Ge3	96h	0.1826(1)	x	0.3705(2)	1	1.11(7)

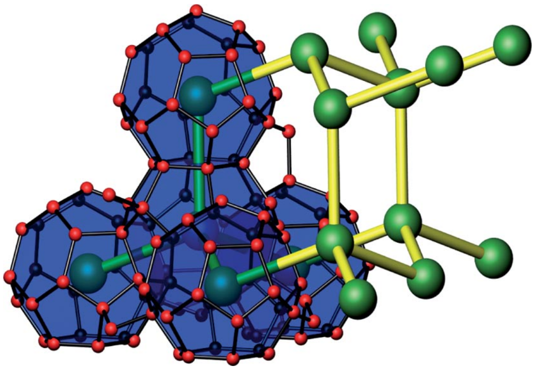

Figure 2. Crystal structure of $K_{8.6(4)}Ge_{136}$ viewed as diamond-like condensation of the K-filled Ge_{28} polyhedra. Red spheres: Ge, green spheres: K. Ge1 atoms that do not belong to the hexakaidecahedra are partially omitted for clarity.

Transmission electron microscopy (TEM) studies confirm the results of the bulk composition analyses and X-ray diffraction studies. The experimental selected area electron diffraction (SAED) patterns for the [110] and [111] zones confirmed the cubic translational symmetry, EDXS on microcrystals identified as the clathrate phase by SAED are in agreement with the composition $K_{8.6(4)}Ge_{136}$. Careful comparison of the HRTEM images with the simulated ones for the relevant crystal orientation [110] also supports the structure model with larger cages that are almost completely filled (Figure 3). The fair quality of HRTEM images may be caused either by incomplete crystallization or by an ongoing decomposition under the electron beam.

DSC measurements performed on closed ampoules, in combination with XRPD analysis, indicate that $K_{8.6(4)}Ge_{136}$ *exothermically* and irreversibly transforms to α-Ge at

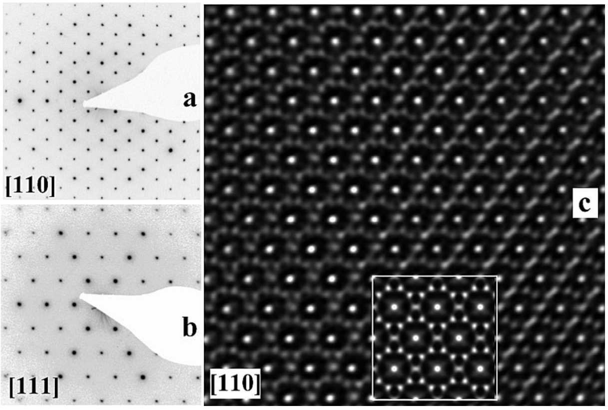

Figure 3. TEM of $K_{8.6(4)}Ge_{136}$: SAED patterns (a) along [110] and (b) along [111]; (c) HRTEM and simulated images for the [110] zone axis (for the used structure model see Table 1).

471 °C. Thus $K_{8.6(4)}Ge_{136}$ is a new *metastable* binary alkali metal germanide. The decomposition temperature compares well with the observed irreversible transformation of the metastable empty clathrate-II Ge (*cF*136) to α-Ge at 420 °C.[9]

Conclusions

The mild oxidation of K_4Ge_9 by the IL (DTAC/$AlCl_3$), followed by annealing at 370 °C, leads to the metastable crystalline clathrate-II $K_{8.6(4)}Ge_{136}$. The previously unknown and unexpected phase transforms to α-Ge at 471 °C and is now available as bulk material. The above results validate the unique opportunities offered by the mild oxidation of Zintl phases and anions in quaternary ammonium-based ionic liquids, as well as the controlled thermal treatment of amorphous oxidation intermediates to form unprecedented structures and metastable phases. Investigations on the oxidation mechanism and the crystal structure of the amorphous intermediate product are in progress.

Experimental Section

Synthesis: K_4Ge_9 was prepared, under Ar, from a stoichiometric mixture of the elements (K 99.95 %, Ge 99.9999 %; ChemPur) in a closed Ta ampoule by inductive heating ($T \approx 1100$ °C). XRPD of the polycrystalline product indicated a pure phase. The IL was prepared from equimolar amounts of dried DTAC and sublimed $AlCl_3$ in glass vessels. Upon addition and stirring of the precursor powders (typical: 85 mg of K_4Ge_9 in 0.5 g of IL) at 50 °C the melt turned brown. The resulting suspension was sealed under Ar in a glass container, slowly heated, and kept at 300 °C for 24 h. The reaction finally leads to the formation of a poorly crystalline black solid, the IL turns clear and colorless. The crude solid product was separated from the IL by several washings with acetone and water, and then dried under vacuum. Subsequent annealing of the crude product under static vacuum, at 370 °C for 2 d, yields polycrystalline, air-stable $K_{8.6(4)}Ge_{136}$. The calculated reaction yield was approximately 70 %, based on the amount of K_4Ge_9 used.

X-ray Powder Diffraction: Measurements were carried out with a STOE-STADI-MP diffractometer (Bragg Brentano geometry, Cu-$K\alpha_1$ radiation). Lattice parameter refinements were performed with LaB_6 as internal standard. Structure refinements were performed by using WinCSD.[17] Relatively high residual values for the data presented in Figure 2, are caused by amorphous contributions of the by-products [$R(P) = 0.167$, $R(I) = 0.138$ for $K_{8.6(4)}Ge_{136}$, $R(I) = 0.099$ for α-Ge].

Electron Microscopy: SAED, HRTEM, and EDXS analyses were performed using a Tecnai F30-G2 electron microscope operated at 300 kV. The starting material was crushed in an agate mortar, dispersed in *n*-butyl alcohol and spread over a carbon film with holes. SAED patterns and HRTEM defocus-series were registered for the directions [110] and [111]. The HRTEM image shown in Figure 2 was taken around SCHERZER optimum defocus ($\Delta f = -50$ nm, specimen thickness ≈ 4.3 nm). Image simulation was performed using the multi-slice formalism of the program package EMS.[18]

Supporting Information (see footnote on the first page of this article): Band structure and chemical bonding of K_8Ge_{136}.

Acknowledgments

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