Soft Preparation of Intermetallic Phases: New Metastable Modification of Germanium in Form of an Empty Clathrate-II

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Interest in empty clathrate-II of silicon and germanium (Fig. 1) is motivated by their predicted wide optical band gaps of the same magnitude as quantum dots and porous Si, making them and their alloys promising materials in optoelectronic devices [1]. Theoretical studies have predicted the stability of $\square_{24}Si_{136}$ and $\square_{24}Ge_{136}$ with respect to the diamond form of the elements, and various methods for their synthesis have been suggested. In contrast to Na_xSi_{136} ($x < 1$), which can be synthesized as a mixture with silicon by thermal decomposition of NaSi in dynamic vacuum [2], all attempts to synthesize an empty or almost empty clathrate-II of germanium failed so far. Attempts to prepare guest-free Si and Ge clathrates using *direct* reactions have been unsuccessful in any case. The advent of low-temperature synthesis has brought new opportunities to the field of materials synthesis and provides new routes to inorganic solids, which are usually prepared by high-temperature reactions. The here reported synthesis of empty clathrate $\square_{24}Ge_{136}$ through oxidation of Ge_9^{4-} Zintl anions in ionic liquids (IL's) under ambient conditions demonstrates the potential of IL's as unique media for the reactions of intermetallic phases.

Ionic liquids of organic salts and their mixtures have unique properties, such as negligible vapor pressure, low viscosity, high thermal, chemical and electrochemical stability, and differentiated miscibility with organic compounds, that make them potentially useful solvents for inorganic synthesis, particularly in the assembly and polymerization of inorganic units into low-density solids. Chemical studies on alkali-metal Zintl phases containing Ge_9^{4-} clusters [3, 4] showed a step-wise oxidative coupling of Ge_9^{n-} ($n = 2 - 4$) anions in amine solvents that culminates in the formation of linear polymers of vertex-linked clusters ${}^{1}_{\infty}[Ge_9^{2-}]$[5, 6]. Further oxidation of the anionic polymers was suggested as a promising route to new elemental Ge structures.

A controlled oxidation of Na_4Ge_9 was performed at 300 °C in an IL composed of dodecyltrimethylammoniumchloride (DTAC) and aluminum trichloride (1:1 molar ratio). The high-yield reaction between the Ge_9^{4-} anions and DTAC follows the Hofmann elimination mechanism [7] and results in the formation of a dark grey polycrystalline product:

$$4[CH_3(CH_2)_{11}N(CH_3)_3]^+ + Na_4Ge_9 \rightarrow 9Ge^0 + 4CH_3(CH_2)_9CH{=}CH_2 + 4N(CH_3)_3 + 2H_2 + 4Na^+$$

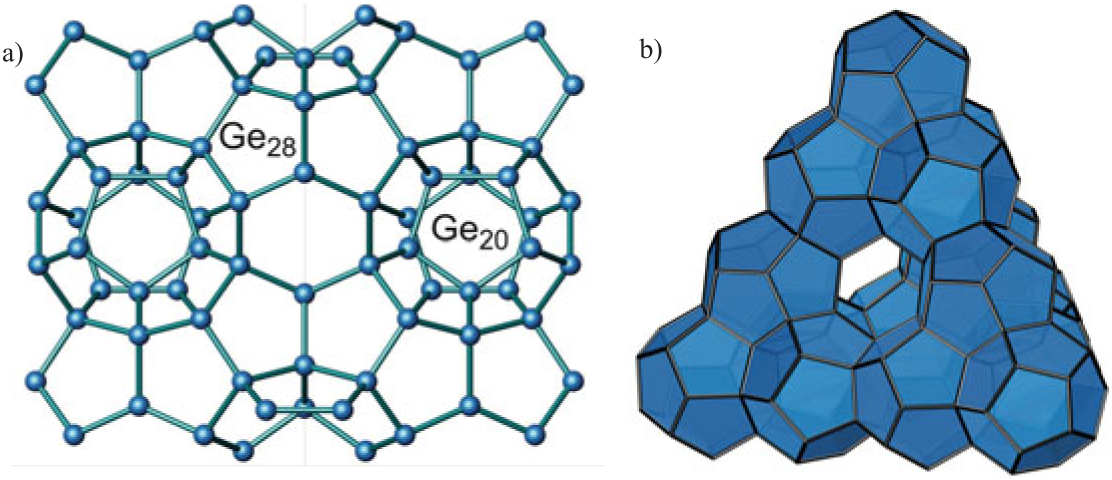

Fig. 1: (a) Unit cell of clathrate-II $\square_{24}Ge_{136}$ viewed along [110]. The crystal structure contains two kinds of basic motifs: distorted pentagon dodecahedra with 20 Ge atoms and hexakaidecahedra with 28 Ge atoms. (b) 16 distorted pentagon dodecahedra, which are connected by common faces, built up a super-tetrahedron whose edges run parallel to the face diagonal of the cubic unit cell.

X-ray powder diffraction patterns of the polycrystalline product were completely indexed with the face-centered cubic lattice and a lattice parameter of $a = 15.2152(1)$ Å, which is notably smaller than those for $\mathrm{Cs_8Ge_{136}}$ ($a = 15.329$ Å) [8] and $\mathrm{Cs_8Na_{16}Ge_{136}}$ ($a = 15.480(1)$ Å) [9, 10]. Full-profile refinement of the crystal structure from powder diffraction data confirmed the clathrate-II germanium framework (space group $Fd\bar{3}m$). Within the e.s.d. the cationic positions were found to be empty [11]. High-resolution transmission electron microscopy (HRTEM) showed the product — being single phase based on X-ray powder diffraction — contained one major crystalline phase ($\square_{24}\mathrm{Ge}_{136}$) and two minor-phases, one being amorphous and one crystalline. The selected-area electron diffraction (SAED) patterns confirmed the cubic symmetry and unit cell parameters of the clathrate-II structure (Fig. 2). The agreement between experimental and simulated images (Fig. 3) was rather good, thus supporting the results of the X-ray crystal structure refinement. However, the complete absence of sodium in the cages of the structure cannot doubtlessly be deduced from HRTEM. Only investigations by electron energy-loss spectroscopy (EELS) revealed the absence of Na in the clathrate phase: no Na-*K* edge at 1072 eV was observed in the EEL spectra (Fig. 4). On the other hand, a very weak Na-*K* signal appeared in the EEL spectra of the amorphous Ge phase. Thus, the residual Na of the bulk material is mainly localized in the amorphous minor phase and the cages of crystalline $\square_{24}\mathrm{Ge}_{136}$ are essentially empty. DSC analysis showed that on heating under inert conditions $\square_{24}\mathrm{Ge}_{136}$ is exothermically and irreversibly converted to the cubic α-Ge (diamond structure) at 420 °C. $\square_{24}\mathrm{Ge}_{136}$ is a diamag-

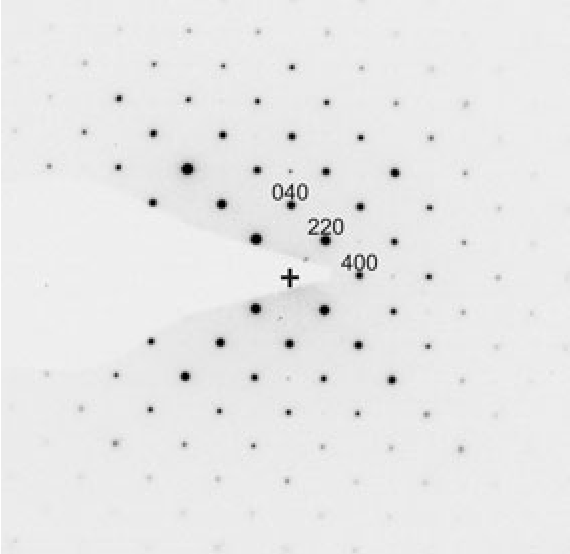

Fig. 2: Selected-area electron diffraction pattern of clathrate $\square_{24}Ge_{136}$ for the [100] zone axis. SAED patterns were also recorded in crystal orientations [110], [111], [112], and [211] – all confirming the cubic symmetry and unit cell parameters determined by XRPD.

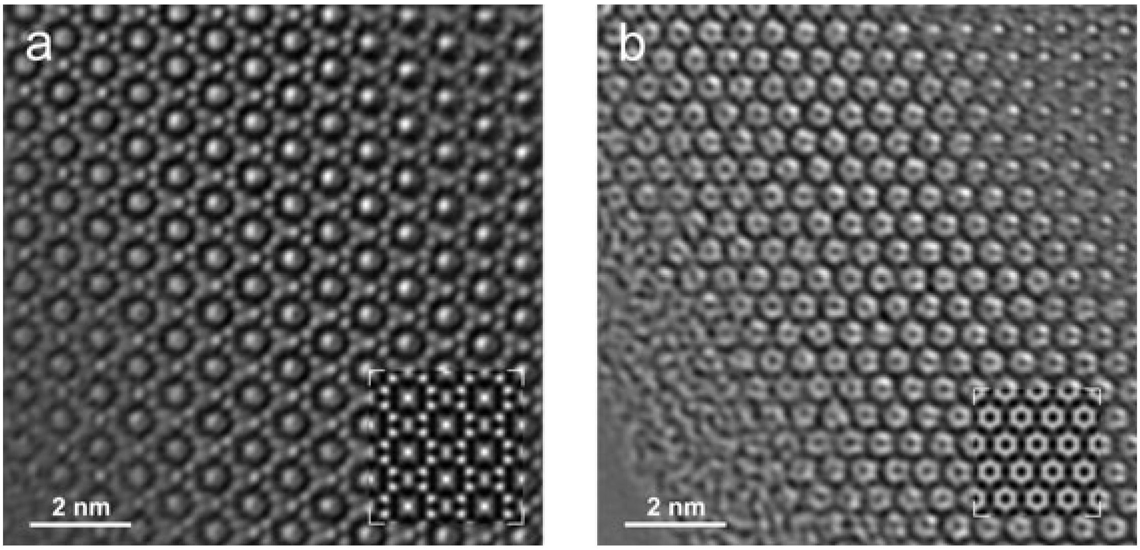

Fig. 3: High-resolution transmission electron micrograph of clathrate $\square_{24}Ge_{136}$ taken around SCHERZER optimum focus for zone axes (a) [110] and (b) [111]. Simulated images (multi-slice formalism) are inserted; defocus: $\Delta f = -50$ nm, specimen thickness: (a) $t = 4.3$ nm and (b) $t = 5.3$ nm. The Tecnai G2-F30 electron microscope with super-twin lens ($C_S = 1.2$ mm) was operated at 300 kV (point resolution 0.2 nm).

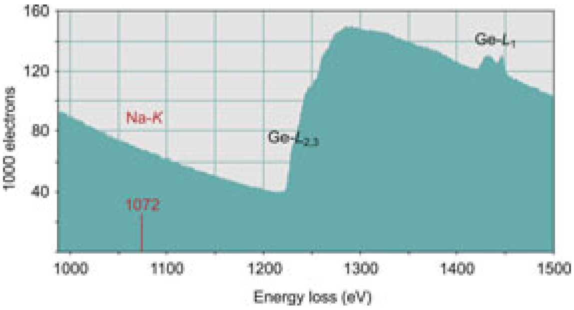

Fig. 4: Electron energy-loss spectrum of a $\square_{24}Ge_{136}$ *microcrystallite (in [100] orientation) showing* $L_{2,3}$ *and* L_1 *edges of germanium at 1217 eV and 1414 eV, respectively. The Na-K edge should appear at 1072 eV.*

netic semiconductor as indicated by magnetic susceptibility and transport property measurements, in agreement with previous band structure calculations and chemical bonding descriptions [12].

The empty clathrate-II $\square_{24}Ge_{136}$ (Fig. 1) is an open, covalently bonded 3D network of tetrahedrally coordinated Ge atoms forming pentagon-dodecahedral Ge_{20} and hexakaidecahedral Ge_{28} cages. Each unit cell contains 16 pentagon dodecahedra and 8 hexakaidecahedra, which provide space for 24 cage positions in a completely filled clathrate. Consequently, the empty clathrate-II is best described by the formula $\square_{24}Ge_{136}$. The average Ge–Ge distance in $\square_{24}Ge_{136}$ is 2.453 Å and closely resembles the bond distance in α-Ge (2.446 Å). The smaller cell volume of the $\square_{24}Ge_{136}$ in comparison to the known filled clathrates is also consistent with an empty clathrate-II model: shorter Ge–Ge distances result from empty antibonding states as compared to the filled clathrate-II model where the electrons from the cation supposedly occupy the Ge–Ge antibonding bands [8]. The significant difference in the unit cell parameters between Na-filled and empty $\square_{24}Ge_{136}$ clathrates is in contrast to Na_xSi_{136} where the unit cell volume does not appreciably change with filling [10].

The oxidation of Zintl anions to form a metastable crystalline phase with novel structural, chemical and physical properties in bulk quantities was demonstrated. We are currently extending the soft chemical synthesis as a general route to novel silicon and germanium structures, as well as using other soluble Zintl phases and anions. It is worth noting that the scalability of a solution method provides the possibility of processing novel clathrate materials for different applications, as e.g. thin film fabrication.

References

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[11] Crystallographic information: Space group $Fd\bar{3}m$, a = 15.2152(1) Å, 8Ge1 in 8a 1/8 1/8 1/8, B_{iso} = 2.04(2) $Å^2$; 32Ge2 in 32e x x x, x =0.2174(1), B_{iso} = 1.79(2) $Å^2$; 96 Ge3 in 96g x x z, x = 0.18291(6), z = 0.3704(1), B_{iso} = 1.67(2) $Å^2$; 0.2(4) Na1 in 16c 0 0 0; R_{Bragg} = 0.080, $R_{Profile}$ = 0.138 for 130 reflections with $\sin(\Theta/\lambda) \leq 0.530$; Cu-$K_\alpha$ radiation. All crystallographic calculations were performed with WinCSD program package. [*L. G. Akselrud, P. Yu. Zavalii, Yu. Grin, V. K. Pecharsky, B. Baumgartner and E. Wölfel*, Mater. Sci. Forum **133-136** (1993) 335.]
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