The Role of Ionic Liquids in the Preparation of Intermetallic Clathrates and Related Element Modifications

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Common synthesis methods for intermetallic phases involve crystallization from the melt or diffusion-controlled solid-state reactions. However, these methods are rarely suitable for the preparation of phases with low temperature stability or metastable phases. The development of alternative preparation methods being applicable at low temperatures is therefore of high value. In this regard a preparation route using redox reactions at relatively low reaction temperatures has opened new perspectives. The metastable germanium allotrope Ge(cF136) with a guest-free clathrate-II crystal structure was obtained by oxidation of $Na_{12}Ge_{17}$ in the ionic liquid (IL) DTAC/AlCl$_3$ (1:1)[1] at 300 °C [1] using a reaction setup sketched in Figure 1a. Subsequently, the metastable clathrate-II $K_{8.6}Ge_{136}$ was prepared in a similar way from K_4Ge_9 as the precursor [2].

Optimization of Reaction Conditions and Development of Gas-Solid Reactions

When aiming for the preparation of crystalline phases, a drawback of the redox reactions in the IL became obvious: Considerable fractions of X-ray amorphous by-products were formed, leading to significant background scattering in the X-ray powder diffraction patterns of the final products [3,4]. In order to optimize the reaction conditions, the thermal stability and reactivity of the ionic liquid was studied in more detail [3]. It turned out that during the reactions described above, the IL entirely decomposed within short times. This finding contradicts the original conception that a decomposition of the IL would only be caused by the reaction with the precursor, while the excess part of the IL would behave inert during the heat treatment [1]. Hence, the self-decomposition products of the IL also had to be taken into account for evaluating the overall reaction with the precursor.

In order to study the influence of the gaseous decomposition products exclusively, the IL DTAC/AlCl$_3$ (1:1) was heated spatially separated from the precursor $Na_{12}Ge_{17}$ in an otherwise unchanged reaction setup (Fig. 1b). Astonishingly, a

well-crystalline clathrate-II product Na_xGe_{136} was obtained making use of the gas-solid reaction, while the yield of X-ray amorphous by-products was negligible. Moreover, by varying the composition of the DTAC-based gas source, the reaction conditions turned out to be tunable [3,4]. At optimized conditions (DTAC/MgCl$_2$ (2:1), 12 days, 280 °C) the oxidation of $Na_{12}Ge_{17}$ resulted in a well-crystalline Ge(cF136) product with a low content of impurities [3]. This product was suitable as a starting material, e. g., for the high-pressure transformation to the new germanium allotrope Ge(hR8) [5]. Only recently, the electrochemical insertion of Li [6] into Ge(cF136) was *in situ* monitored by synchrotron X-ray powder diffraction experiments. Moreover, gas-solid reactions using DTAC-based systems succeeded in the preparation of well-crystalline $K_{8-\delta}Ge_{44+y}$ type-I clathrates with compositions deviating from those of products obtained by any other method [3].

The Principles of the Gas-Solid Reactions

The application of DTAC-based systems as gas-sources for redox reactions raised several questions. The most prominent one addresses the nature of the oxidizing agents and the redox reactions which can be expected.
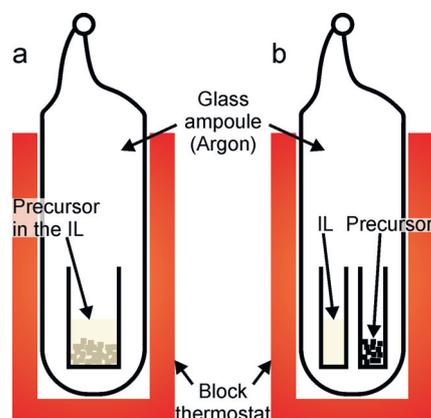

Fig. 1: Setup for the oxidation of intermetallic precursors (a) in a liquid-solid reaction with the IL DTAC/AlCl$_3$ (1 : 1 molar ratio) and (b) in a gas-solid reaction with the gaseous decomposition products of the IL.

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[1] DTAC = *n*-dodecyltrimethylammonium chloride
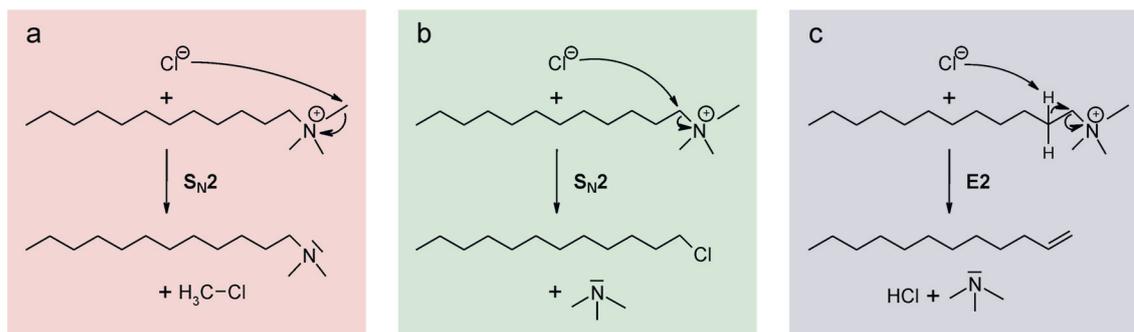
Fig. 2: Reaction paths of the Cl⁻-induced thermal decomposition of n-DTA$^+$ ions: (a), (b) nucleophilic substitutions with S$_N$2 mechanism and (c) Hofmann elimination with E2 mechanism.

Hence, an extensive study was performed on the thermal decomposition behavior of DTAC and its "neutral" ILs [7] DTAC/MgCl$_2$ (2:1) and DTAC/AlCl$_3$ (1:1) using experimental conditions resembling those of the reactions with precursors [3, 4]. The gaseous decomposition products were subjected to *in situ* analysis using a TG-MS setup for the handling of air-sensitive samples [8]. Furthermore, the solid precipitates from the gas-phase formed during the heat treatments at colder zones of the reaction ampoules (Fig. 1) were investigated *ex situ* by X-ray powder diffraction.

The experiments revealed that the effective decomposition of DTAC-based systems can be attributed to three competing decomposition reactions of the n-DTA$^+$ ions, which are induced by Cl⁻ ions acting either as a nucleophile or as a base (Fig. 2). The relevant oxidizing agents evolved by decomposing n-DTA$^+$ were concluded to be CH$_3$Cl, C$_{12}$H$_{25}$Cl and HCl. This explains why the gas-solid oxidation of the precursors always yielded metal chlorides as the solid coupling product. Possible redox reactions of a precursor with such chlorides are sketched in Figure 3. While the protons of HCl are reduced to H$_2$, the organic chlorides may similarly react in Wurtz-analogous reactions forming alkanes. For higher alkyl chlorides as C$_{12}$H$_{25}$Cl not only coupling to C$_{24}$H$_{50}$ but also competing reactions such as the formation of C$_{10}$H$_{21}$–CH=CH$_2$ and C$_{12}$H$_{26}$ might occur.
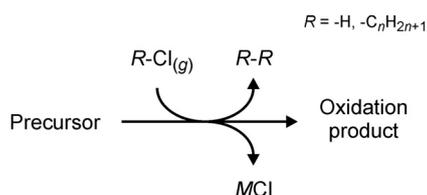
Chloroalkanes and HCl, which were identified as oxidizing agents in gas-solid reactions with DTAC based systems have proven to be applicable also in pure form: Gaseous HCl was used, e. g., in the oxidative preparation of silicon clathrates [9], while 1,6-dichlorohexane was successfully applied in gas-solid reactions yielding K$_{8-\delta}$Ge$_{44+y}$ [3].

The relative share of the reaction paths depicted in Figure 2 to the overall decomposition of n-DTA$^+$ was found to depend on the composition of the DTAC-based system. Also, the overall reaction rate at a given temperature decreased in the order DTAC – DTAC/MgCl$_2$ – DTAC/AlCl$_3$. As the decomposition reactions of n-DTA$^+$ have second order kinetics, the latter is explained by decreasing concentrations of free Cl⁻ ions in the liquid phase due to the formation of chloro complexes of which AlCl$_3$ yields the most stable ones. Experimentally, the different decomposition rates have proven to be useful for controlling the oxidation of a precursor at a given temperature. It was concluded that the oxidation products formed from a precursor predominantly depend on the different *in situ* overall pressures of the oxidizing agents in the reaction ampoules. The actual kind of the oxidizing agents involved seems to be of minor importance as they can be considered as similarly reactive towards the investigated precursors [3, 4].

Liquid-Solid Reactions Reinvestigated
Originally, the oxidative route to clathrate phases, based on heating dispersions of precursors in the IL DTAC/AlCl$_3$ (1:1) (Fig. 1a). The finding that clathrates also form in heterogeneous gas–solid reactions evokes the question, whether the oxida-
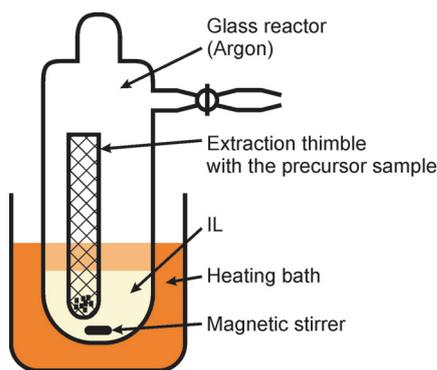

Fig. 3: Oxidation of an intermetallic precursor by HCl or organic chlorides.

Fig. 4: Reaction setup for investigations on the solubility of K_4Ge_9 in the ionic liquid DTAC/AlCl$_3$ (1:1).

tion of a precursor in the ionic liquid comprises a solution step as previously assumed [1]. The solubility of germanide precursors in the IL was therefore reinvestigated [3]. K_4Ge_9, which is well known to dissolve in amines [10], was used as model compound. The experiments were carried out at temperatures below 170 °C so that the thermal decomposition of the IL is negligible [3, 4]. An experimental setup used in these investigations is sketched exemplarily in Figure 4. Here, the IL was stirred vigorously, facilitating a continuous flow through a glass fiber extraction thimble containing K_4Ge_9. This way, possibly dissolved species would have been transported away from the precursor, and their oxidation products would have been permitted to precipitate outside of the extraction thimble. But, after a reaction time of 14 h at 170 °C, chemical analysis (OES) could not detect K or Ge in the IL. Also, oxidation products of the precursor had not precipitated outside of the extraction thimble. The oxidation of the precursor was indicated by the characteristic reflections of KCl in the X-ray powder diffraction pattern of the dark gray solid remaining *inside* the extraction thimble albeit crystalline KGe$_x$ phases had not formed. These XRPD findings agree with previous results from reactions at such low temperatures [3].

The experiments showed that neither K_4Ge_9 nor KCl significantly dissolve in the IL DTAC/AlCl$_3$ (1:1). Moreover, K_4Ge_9 is already oxidized at temperatures well below the thermal decomposition of the IL, so that a direct reaction of the IL with the precursor is evidently proceeding heterogeneously at the surface of the precursor particles. As originally suggested, the acidic protons of *n*-DTA$^+$ should act as oxidizing agents [1, 3]. Towards higher reaction temperatures, thermal decomposition products of the IL will contribute to the oxidation of the precursor as well.

Summary

The gas-solid oxidation of precursor phases proceeding in closed setups containing DTAC-based systems is explained by the presence of gaseous alkyl chlorides and HCl originating from the thermal decomposition of DTAC. The knowledge of these oxidizing agents and their advantageous utilization provides the base for further developments of the redox preparation method and its application in technical scale. So far, the oxidation of precursors has been performed using dispersions in the IL DTAC/AlCl$_3$ (1:1). The presented results clearly show that the oxidation of K_4Ge_9 in this case proceeds *heterogeneously* as well and a significant solubility is ruled out.

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