

ThermoPhIL: Thermochemical Investigations of Phase Formation Processes in Ionic Liquids

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During the last decade, a great progress has been achieved in the variety of application of ionic liquids in inorganic synthesis [1, 2]. The advantage of ionic liquid based synthesis is mainly founded on low melting temperatures of IL. Despite the low temperature, high reactivity of inorganic solids in ILs can be observed. Thus, soft synthesis conditions can be applied in synthesis and even low temperature metastable materials are attainable [3]. Nevertheless, systematic investigations with the conception of ionic liquids and ionic liquid mixtures as flux systems with temperature and composition dependent physico-chemical properties are lacking to date.

As a main topic, the formation of element allotropes and compounds of group XV and XVI elements is presented. As almost all the elemental syntheses succeeded by an electrochemical reduction of the binary oxides, the idea grew to estimate electrochemical potentials [4] of oxidic precursors for directed reduction towards the elements. For this purpose, complex CalPhaD modeling has been realized to account for both complex gas phase equilibria which lead to defining $p(O_2)$, and possible sublimation reactions of elements or compounds ($p(i)$). In accordance to thermochemical modeling, the reduction of the oxides of As, Sb, Bi, Se, and Te succeeds by application of the reaction system $NaBH_4/[C_4mim]BF_4$. The reduction also proceeded also without reduction agent in the temperature range $\vartheta = 225\text{ °C} \dots 300\text{ °C}$. Thus, the ionic liquid itself functioned as a reduction agent.

Referring to this finding, we analyzed the thermal behavior of the applied IL. Problematically, commonly applied methods for determination of thermal decomposition temperature (TG/DSC) vary in a range of up to 50 K. Thus, we have applied and optimized a kinetic model for determination of time dependent thermal stability of ionic liquids: Maximum Operation Temperature (MOT) [5]. The MOT value describes the maximum temperature (with a mass loss less than 1%) for application of an ionic liquid in a given period of time. As a conclusion, the thermal stability of IL is much lower as expected based on standard TG experiments and the thermal decomposition of IL can influence the reaction mechanism of materials synthesis.

Furthermore, reaction systems in IL`s have been investigated, where the optimum reaction temperature is determined by the composition of the flux system and the melting temperature of the respective mixture. Thus, reaction systems of ionic liquid halido metalates (here $[C_4mim]AlCl_4$) with higher contents of the metal salt ($AlCl_3$) usually require higher reaction temperature. Almost equimolar mixtures ($[C_4mim]AlCl_4$) are applicable near room temperature, due to their low melting point.

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