

Priority Programme

“Material Synthesis near Room Temperature”



Project Description – Project Proposal

Chalkogenide-based Ionic Liquids in the Synthesis of Metal Chalkogenide and Interchalkogenide Materials near Room Temperature

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Summary of proposal

The project investigates the application of ionic liquids (IL) comprising chalcogen-based anions of the hydrochalcogenide [EH], trimethylsilylchalcogenide [E-TMS] or polychalcogenide type [Ex] (E = S, Se, Te) in the synthesis of selected 2D- and 3D-metal chalcogenide or poly- and interchalcogenide materials. This research will demonstrate a clear benefit of using such highly reactive synthons for chalcogen transfer, that combine easy access, highest purity, perfect solubility in organic co-solvents, low melting points (in some cases) and highest reactivity towards electrophiles and Lewis acids. A first strategy follows up protolysis reactions of selected metal organyls and amides in ionic liquids Cat [EH] (E = S, Se), a second complementary strategy the anion metathesis of metal halides dissolved in Cat [E-TMS] and Cat [EH] ILs. In this respect, selected metal precursor compounds of the p-block, Ga(III), In(III), In(II) and Sn(II), are planned to be compared in their reactivity pattern with selected precursors of the f-block elements, Ln(II) and Ln(III). New classes of thermally labile chalcogenido organometallates [(RxM)yEz]ⁿ⁻ (M = Ga, In, La and Ln; E = S, Se) and of trimethylsilylchalcogenido-metallates [M(E-TMS)₄]⁻ (M = Ga, In, La) will be accessible. They are labile intermediates in their conversion into semiconducting materials ME, M₂S₃ and ME₂ at room temperature or slightly above. Room temperature IL reactions allow the isolation of novel tin(II) and tin(IV) precursor compounds, Cat[SnE₂] and Sn(E-TMS)₄ (E = S, Se), awaiting their condensation to SnE and SnE₂ semiconducting materials. Reaction of [NH₄]₂[MoS₄] with methylcarbonate ILs Cat[MeCO₃] offers access to intermediates Cat₂[MoS₄], that are planned to be converted to MoS₂ via two strategies: 1) thermolysis in a IL flux and 2) reaction with electrophiles followed by reductive elimination of disulfides RSSR. A third strategy investigates the thiolysis of [MoX₄] complexes in Cat[SH] or Cat[S-TMS] ILs. Finally, the benefit of chalcogenide ILs in low-temperature syntheses of chalcogen-rich polychalcogenide, interchalcogenide and interchalcogen materials is planned to be explored.