Materials Based on Heavy Analogues of Silicates, Silicones, or Silicides

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The tuning of materials properties can be achieved in many different ways, including post-synthetic treatment like dimensional reduction by mechanical stress.[1] Chemical methods address variations of compositions and structures by suitable synthetic approaches. In our work, we aim at a controlled diversification by the use of binary precursor units that are combined with a third component to form ternary cluster or network compounds.[2] The precursors represent heavy homologues of the *ortho*-silicate anion, $[SiO_4]^{4-}$, or of silicone building unit like $[RSiO_3]^{2-}$ (R = org. group), or they are isoelectronic analogues of the smallest silicide anion, Si_4^{4-}. Heavy atom or isolobal replacement of the Si or O atoms not only affects the reactivity and electronic properties of the precursor molecules, but also leads to dramatic changes of geometric and electronic structures of the reaction products. Recent examples comprise alkali metal superion conductors like $Li_{10}Sn_2PS_{12}$ or $Na_{11}SnP_2S_{12}$,[3] amorphous molecular solids with extreme non-linear optical properties like $[(RT)_4S_6]$ (R = organic group, T = Si, Ge, Sn)[4] and very uncommon bi- and trimetallic Zintl clusters like $(Ge_4Bi_{14})^{4-}$, $[Ta@Ge_8As_6]^{3-}$, or $[Cd_3(Ge_3P)_3]^{3-}$.[5]

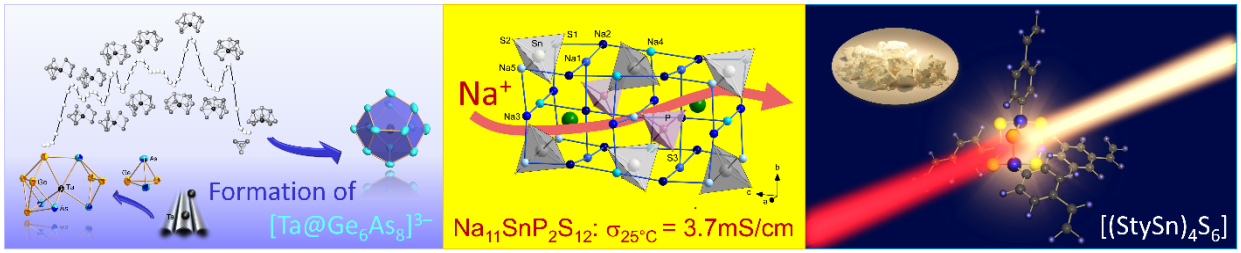

Figure 1. Compounds formed with heavy analogues of Si_4^{4-}, $[SiO_4]^{4-}$, or $[RSiO_3]^{3-}$ (from left).

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