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Systematic Investigations on the Transition from Zintl Phases to Intermetallics

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Abstract

The work presented here is a compilation of syntheses and characterizations of intermetallic phases formed between elements of the 13th group (the aluminum group), the 14th group (the silicon group), alkaline metals, and alkaline-earth metals. The primary aspect was to investigate the electronic properties of compounds formed by elements separated by the Zintl border, group 13 or triel and group 14 or tetrel elements, respectively. While the majority of the compounds of triels with more electropositive cations fall into the class of intermetallics, the corresponding tetrel compounds typically belong to the valence or Zintl phases.

The following new compounds were synthesized and structurally characterized: **α-** and **β-Li_5AlSi_2**, **$Li_{4+x}Al_{2-x}Si_2$** ($x \sim 1$), **α-** and **β-Li_5AlGe_2**, **$Li_{4+x}Al_{2-x}Ge_2$** ($x \sim 1$), **$Li_{4+x}Ga_{2-x}Si_2$** ($x \sim 1$), **α-Li_5GaGe_2**, **$Li_{4+x}Ga_{2-x}Ge_2$** ($x \sim 1$), **Li_5AlSn_2**, **$Li_xCaAl_{1-x}Si$** ($x \sim 0.5$), **$Li_xCaAl_{1-x}Ge$** ($x \sim 0.5$), **$Li_xSrAl_{1-x}Si$** ($x = 0.5$), **$Li_xSrAl_{1-x}Ge$** ($x = 0.5$), **$Li_{2+x}Sr_2Al_{6-x}Si_6$** ($x \sim 2.8$), **$Li_{3+x}Sr_5Al_{16-x}Si_{12}$** ($x \sim 6.2$), and **SrGaSi**.

Measurements of the thermal behaviour, magnetic properties, and electrical conductivity were performed on many of these compounds whenever possible. Quantum mechanical calculations, especially of density of states (DOS), band structures, and of the electron localization function (ELF), were used to investigate the electronic structure and the bonding characteristics of these phases.

Structures and structural relationship of the ternary compounds found in the Li/Tr/Tt systems were very intensively investigated. All the synthesized compounds have almost the same compositions Li_5TrTt_2. Three different structure types were found. The tetragonal α-Li_5TrTt_2 (Tr = Al, Ga; Tt = Si, Ge, Sn), which shows a cristobalite-like network built of the Tr-Tt elements; the cubic β-Li_5TrTt_2 (Tr = Al, Ga; Tt = Si, Ge), closely related to the tetragonal structure; and the hexagonal $Li_{4+x}Tr_{2-x}Tt_2$ ($x \sim 1$) (Tr = Al, Ga, Tt = Si, Ge), which is a coloured version of graphite with layer built of the tetrel element sites and triel/lithium mixed occupied positions while in addition lithium is

intercalated between the layers. These compounds show interesting phase relationships. In fact the last two structures can be described as **high temperature modifications** of the **α-Li_5TrTt_2 phase**. The phase transition between the α-Li_5TrTt_2 and β-Li_5TrTt_2 was investigated by difference thermal analysis (DTA) and high temperature X-ray powder diffraction experiments for the Al/Si, Al/Ge, Ga/Ge compounds. The hexagonal $Li_{4+x}Tr_{2-x}Tt_2$ phases can be described as the γ-modifications, because the composition is close to Li_5TrTt_2. This phase was very often found together with the α-Li_5TrTt_2 modifications. The hexagonal $Li_{4+x}Tr_{2-x}Tt_2$ phases exist within a phasewidth of, yet, unknown range. Interestingly the double nature semimetal/metal of the electronegative elements becomes evident by analysing the physical properties of the α- and the γ-phases: the first are semiconductors with the more or less expected exception of the tin compound, the second are all metals.

In all the newly discovered quaternary phases, interestingly, the aluminum atoms share always positions with lithium atoms in a more or less statistical way. In the quaternary Li/Sr/Al/Tt systems (Tt = Si, Ge) three new structure types were discovered. The first structure, $Li_xSrAl_{1-x}Tt$ (x = 0.5, Tt = Si, Ge), presents layer of the tetrel-Al/Li atoms and is isostructural and isoelectronic to the NaAlSi compound. The second compound $Li_{2+x}Sr_2Al_{6-x}Si_6$ (x ~ 2.8) crystallizes in a new structure type, which can be seen as an intermediate between the well known $BaAl_4$ structure and the first phase. The third phase $Li_{3+x}Sr_5Al_{16-x}Si_{12}$ (x ~ 6.2) presents an interesting zeolite-like network built of the silicon, aluminum and mixed occupied positions Al/Li. The channels are filled by strontium and lithium atoms. All these four new compounds are, as expected, metals.

In the quaternary Li/Ca/Al/Tt (Tt = Si,Ge) systems two new, isostructural, compounds were found. The $Li_xCaAl_{1-x}Tt$ ($0.4 < x < 0.6$, Tt = Si, Ge) phases although almost isoelectronic to the strontium compounds crystallize in another structure type. The phasewidth was determined. The silicon compound presents a superstructure, which was intensively investigated. However, also there remain some blocks where aluminum/lithium positions are mixed occupied. Also these new phases are metals.

The ternary phase SrGaSi crystallizes in the AlB_2 structure type, and, like recently discovered for other isostructural compounds, becomes superconducting at temperatures below 4.5 K. Therefore, the electronic structure was intensively studied. The planar Ga/Si layers are characterized by half filled π^*-states, the compound is therefore expected to be Pauli paramagnetic and a metal.