**Li$_{13.7}$Rh$_8$Si$_{18.3}$ – A Non-Centrosymmetric Variant of the R-Phase Structure**

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The silicide Li$_{13.7}$Rh$_8$Si$_{18.3}$ was synthesized from the elements in a sealed niobium ampoule at 1370 K followed by slow cooling. The sample was studied by powder and single-crystal X-ray diffraction. Li$_{13.7}$Rh$_8$Si$_{18.3}$ crystallizes with a non-centrosymmetric occupancy variant of the R-phase structure Mg$_{32}$(Al, Zn)$_{49}$: $I_{23}$, $a = 1306.9(2)$ pm, $wR^2 = 0.0447$, 1286 $F^2$ values, and 53 variables. Striking structural motifs of the Li$_{13.7}$Rh$_8$Si$_{18.3}$ structure are $M_{12}$ icosahedra and $M_{60}$ buckyball-type clusters ($M = Si + Rh$), both partially built up from mixed-occupied sites.

**Key words:** Lithium, Silicide, Group-Subgroup, Crystal Structure

**Introduction**

Lithium transition metal (T) stannides have intensively been studied in recent years with respect to their crystal chemistry and lithium mobility, aiming for electrode materials for lithium batteries [1 – 24]. The use of intermetallic lithium compounds instead of elemental lithium has two main reasons, (i) the dendrite growth upon lithium reduction is reduced and (ii) the charge transfer from lithium to a polyanionic network strongly increases the melting point of the materials which is a significant safety aspect. To give an example, from elemental lithium to Li$_{22}$Sn$_5$, the melting point increases from 181 to 783 °C [25]. Similar trends occur for ternary compounds.

The structural chemistry of the Li$_x$T$_y$Sn$_z$ stannides has a common principle. The transition metal and tin atoms build up two- or three-dimensional polyanionic, covalently bonded [T$_y$Sn$_z$]$^{δ−}$ networks which are separated and charge-balanced by the lithium ions. The charge transfer from lithium to the transition metal and tin atoms enables the formation of the polyanions. Most compounds show a precise composition, while extended solid solutions have been observed for the series Li$_{3−x}$Pt$_2$Sn$_{3+x}$ [14], Li$_{42.5}$Pd$_2$Sn$_{58.5}$ [19], and Li$_x$T$_y$Sn$_{7−x}$ (T = Rh, Ir) [21]. Mixed-occupied sites and/or vacancies are a good prerequisite for lithium mobility. Such sites have more frequently been observed for the family of lithium transition metal silicides. So far the silicides Li$_5$Ni$_4$Si$_7$ [26], Li$_{13}$Ni$_{40}$Si$_{31}$ [27], Li$_{77−x}$Ni$_{20}$Si$_{135−y}$ (x = 2; y = 7) [28], LiCuSi [26, 29], LiCu$_2$Si [1, 3], LiCu$_4$Si$_2$ [30], Li$_{119}$Cu$_{145}$Si$_{177}$ [31], Li$_{113}$Cu$_{54}$Si$_{57}$ [32], Li$_{7}$Cu$_{2}$Si$_{5}$ [33], Li$_2$ZnSi [34, 35], LiRh$_2$Si [36], Li$_{113}$Pd$_{12}$Si$_{12}$ [37], LiPdSi$_3$ [38], Li$_8$Ag$_2$Si$_5$ [29], Li$_8$Au$_2$Si$_5$ [29], Li$_2$AuSi [2], and LiRh$_2$Si$_2$ [39] have been reported. Especially the nickel- and copper-containing phases exhibit large unit cells with substantial disorder. In continuation of our phase analytical investigations of the Li-Rh-Si system, besides LiRh$_2$Si$_2$ [39] and Li$_3$Rh$_4$Si$_4$ [40], we have obtained a new complex silicide Li$_{13.7}$Rh$_8$Si$_{18.3}$, which is structurally related with the R-phase structures [26, 41 – 50], originally determined for Mg$_{32}$(Al, Zn)$_{49}$ [41, 42], and later on for the lithium-containing phases Li$_2$CuAl$_5$, Mg$_{63}$(Zn, Al)$_{37}$ [49]. Herein we report on the synthesis and structure of Li$_{13.7}$Rh$_8$Si$_{18.3}$.

**Experimental Section**

**Synthesis**

Starting materials for the preparation of the Li$_{13.7}$Rh$_8$Si$_{18.3}$ sample were lithium rods (Merck, > 99 %), rhodium powder (Heraeus, ca. 200 mesh, > 99.9 %) and silicon lumps (Wacker, > 99.9 %). The lithium rods were cut into smaller pieces under dry paraffin oil and subsequently washed with n-hexane. The lithium pieces were kept in Schlenk tubes under argon prior to the reaction. Argon was purified with titanium sponge (900 K), silica gel, and...
molecular sieves. The lithium pieces were mixed with the rhodium powder and the silicon lumps in the 16:9:15 atomic ratio under flowing argon, and then arc-welded [51] in a niobium ampoule under an argon pressure of about 700 mbar. The niobium tube was subsequently enclosed in an evacuated silica tube for oxidation protection. The sample was heated to 1370 K within 5 h and kept at this temperature for 1 h. Thereafter the tube was rapidly cooled to 973 K within 1 h. After three days of annealing at 973 K, the furnace was slowly cooled to r. t. at a rate of 1 K min⁻¹. The sample could readily be separated from the tube. No reaction with the container material was observed. The sample is stable in air for several days and was kept in argon-filled Schlenk tubes for best conservation. Single crystals exhibit metallic lustre and could be easily separated from the bulk material. Powders are dark grey.

**EDX data**

Semiquantitative EDX analyses of the crystal investigated on the diffractometer was carried out with a Leica 420i scanning electron microscope with Rh and SiO₂ as standards. The experimentally observed composition (33±3 at.% Rh: 67±3 at.% Si) was close to the composition obtained from the single-crystal refinement of 30.4 at.% Rh: 69.6 at.% Si. No impurity elements were observed. The uncertainty of the semiquantitative analyses arises from the irregular surface of the crystal. The lithium content could not be determined via EDX (detectability limit of the instrument).

**X-Ray diffraction**

The polycrystalline Li₁₃₋₃Rh₈Si₁₈.₃ sample was characterized through a Guinier pattern (imaging plate detector, Fujiﬁlm BAS-1800) with CuKα₁ radiation and α-quartz (α = 491.30, c = 540.46 pm) as an internal standard. The lattice parameter was deduced from a least-squares fit to the powder data. Correct indexing of the pattern was ensured by an intensity calculation [52]. The powder (α = 1306.9(2) pm) and single-crystal (α = 1305.9(2) pm) lattice parameters agreed well.

Well-shaped single crystals of Li₁₃₋₃Rh₈Si₁₈.₃ were isolated from the bulk material under a light microscope, glued to quartz ﬁbres using bees wax and then investigated via Laue photographs on a Buerger camera (white Mo radiation) in order to check their quality. Intensity data of a suitable crystal were collected with graphite-monochromatized MoKα radiation on a Stoe IPDS-II diffractometer in oscillation mode. A numerical absorption correction was applied to the data set. All relevant crystallographic data for the data collection and evaluation are listed in Table 1.

**Structure determination and reﬁnement**

Careful examination of the Li₁₃₋₃Rh₈Si₁₈.₃ data set showed a body-centered cubic cell with low Laue symmetry and no further systematic extinctions, leading to space groups 1̅3m and 123, of which the non-centrosymmetric group was found to be correct during structure reﬁnement. The starting atomic positions of the rhodium and silicon sites were obtained through Direct Methods with SHELXS-


dicating lower scattering power. Consequently, we refined these sites with mixed Rh/Si and Si/Li occupancies. All other sites were fully occupied within two standard deviations and in the final cycles the ideal occupancy parameters were used. Assuming the two mixed-occupied sites we refined a composition $Li_{13.7}Rh_8Si_{18.3}$ for the investigated crystal.

Inspection of the Pearson code (c1160) revealed similarity with the R-phase structures [26, 41 – 50], however, these intermetallics adopt the centrosymmetric space group $I3m$, a supergroup of $I23$. Subsequently we tried to refine the structure also with a centrosymmetric R-phase-related model in space group $Im3$ with mixed-occupied sites. This refinement, however, revealed a strongly enhanced residual $R1$ of 0.1826 for all data, expressing the strong anomalous dispersion contribution of the rhodium atoms. This was a clear hint for the non-centrosymmetry of the structure. Refinement of the correct absolute structure was ensured through a calculation of the Flack parameter [55, 56]. The latter pointed to twinning by inversion. Consequently the inversion twin matrix was introduced and a batch scale factor was refined (Table 1).

A final difference Fourier synthesis revealed no significant residual peaks. The refined atomic positions, displacement parameters, and interatomic distances are given in Tables 2 and 3.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-421555.

Discussion

The ternary silicide $Li_{13.7}Rh_8Si_{18.3}$ crystallizes with a new structure type which can be considered a non-centrosymmetric, ordered version of the R-phase structure [41, 42]. This new ordering variant and the prototype Mg$_3$Al (Al, Zn)$_4$ are related by a group-subgroup scheme (Fig. 1) [57 – 59]. Space group $I23$ is a translationenleiche subgroup of $Im3$. This readily explains the twinning by inversion observed for the investigated crystal. Since $Li_5N_i_4Si_7$ [26] is crystal-chemically better related to $Li_{13.7}Rh_8Si_{18.3}$, the group-subgroup scheme presented in Fig. 1 was worked out for this pair of compounds. The 1:1 Rh/Si ordering on the $M1$ site of $Li_5N_i_4Si_7$ is the main reason for the lowering of the symmetry. This way the 48h site is split into two 24f sites. Furthermore we observe splitting of the 16f lithium site. The mixed-occupied 24h $M2$ site of $Li_5N_i_4Si_7$ remains a mixed-occupied site $M2$ also in $Li_{13.7}Rh_8Si_{18.3}$. In contrast to $Li_5N_i_4Si_7$ we observe a small Si/Li mixed occupancy for one 12e
Fig. 1. Group-subgroup scheme in the Bärnighausen formalism [57 – 59] for the structures of Li5Ni4Si7 [26] and Li13.7Rh8Si18.3. The index for the translationengleiche symmetry reduction (t) and the evolution of the atomic parameters is given. For the mixed-occupied sites in the Li13.7Rh8Si18.3 structure see Table 2.

Fig. 2. Coordination polyhedra in the structure of Li13.7Rh8Si18.3. Site symmetries are given in parentheses. For the mixed-occupied sites M see Table 2.

The coordination polyhedra of the nine crystallographically independent sites are presented in Fig. 2. The lithium atoms have coordination numbers (CN) of 15 (Li3) and 16 (Li1, Li2, Li4). Due to the site splitting in the centrosymmetric space group the coordination polyhedra of Li1 and Li4 are very similar (see also Table 3). Within these polyhedra, the Li–Li distances cover a relatively broad range from 268 to 307 pm. The shorter Li–Li distances are all somewhat smaller than in bcc lithium (304 pm) [60], similar to the situation in LiRh2Si2 (275 pm) [39]. In view of the highly ionic character (and thus small size) of lithium in Li13.7Rh8Si18.3 (vide infra), these interactions may not be considered as bonding.

The shortest interatomic distances in the Li13.7Rh8Si18.3 structure occur between the rhodium and silicon atoms. The atoms Rh, Si1 and Si2 presented in Fig. 2 have CN 12 in the form of strongly distorted icosahedra. This is also expressed by the low
site symmetry 1. The Rh–Si distances range from 239 to 252 pm, close to the sum of the covalent radii of 242 pm [61]. A similar range (244 – 248 pm) has been observed for LiRh₂Si₂ [39]. We can therefore assume substantial covalent Rh–Si bonding in Li₁₃₇Rh₈Si₁₈₃. Besides we observe shorter Si₁–Si₂ distances of 242 and 249 pm. Although both distances are slightly longer than in elemental silicon (235 pm) [60], besides stronger Rh–Si we also observe weaker Si–Si bonding.

Together, the rhodium and silicon atoms build up a complex three-dimensional network. As emphasized in Fig. 3, the structure of Li₁₃₇Rh₈Si₁₈₃ contains a buckyball-type \( M_{60} \) cluster which encapsulates a slightly distorted icosahedron of M₂ atoms. The lithium atoms as the most electropositive part of Li₁₃₇Rh₈Si₁₈₃ will largely have transferred their valence electrons to the rhodium and tin atoms, thus enabling formation of a polyanionic network. To a first approximation we can formulate \([\text{Li13}_7\text{Rh8Si18}_3]^{3+}\). The condensed network of the \( M_{60} \) clusters is shown in Fig. 4.

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References
