

## Zintl anions of silicon in rare earth halides

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In the ‘Jahresbericht 1995’ we reported on boride and boride carbide halides of the rare earth metals. Owing to the electropositive character of the metals, the interstitial B and C atoms, as well as the  $B_x$  and  $B_xC_y$  units are present as anions denoted as A. Several factors influence the nature of the interstitial species A: The number of electrons which can be donated by the  $REX_n$  framework (RE=rare earth metal, X=halogen) determining the A–A bonding, the electronic balance between RE–RE, RE–A and A–A bonding, and the dimensions and distribution of voids in the metal atom arrangement.

So far, the only known compounds with silicon as interstitial atom are  $Gd_4I_5Si$  and  $Gd_3I_3Si$ . Isolated Si atoms center  $Gd_6$  octahedra, similar to carbon in the corresponding carbide halides. Compared to the binary and ternary RE silicides, the variation of the halogen content offers an additional means for fine-tuning the valence electron concentration and hence the nature of the Si Zintl anions. Since the electron transfer to the interstitial Si species is decreased in the halide silicides compared to the binary silicides,

larger  $Si_n$  entities may be formed given appropriate geometrical conditions.

We prepared the novel compounds  $La_3Cl_2Si_3$ ,  $La_6Br_3Si_7$ , REISi (RE=La, Ce, Pr),  $La_4I_3Si_4$  and  $La_5I_3Si_5$  by annealing stoichiometric mixtures of  $REX_3$ , RE and Si in sealed Ta tubes at temperatures of  $\approx 1000^\circ C$  for several days. The compounds were obtained as needles or laths with metallic cluster. Conductivity measurements on pressed or sintered pellets revealed metallic behavior between 5 K and room temperature. The compounds are extremely sensitive towards moisture and ignite explosively upon contact with water.

Figure 6 a)–e) depicts the characteristic building blocks of the structures of these compounds. All Si atoms are coordinated by the RE atoms in a trigonal-prismatic fashion, but the interconnection of the prisms differs in the structures. There are two ways of fusing the prisms to attain optimal space filling, and these differ with respect to the relative orientation of the quasi-threefold axes, which can be parallel (p) or orthogonal (o) to each other.

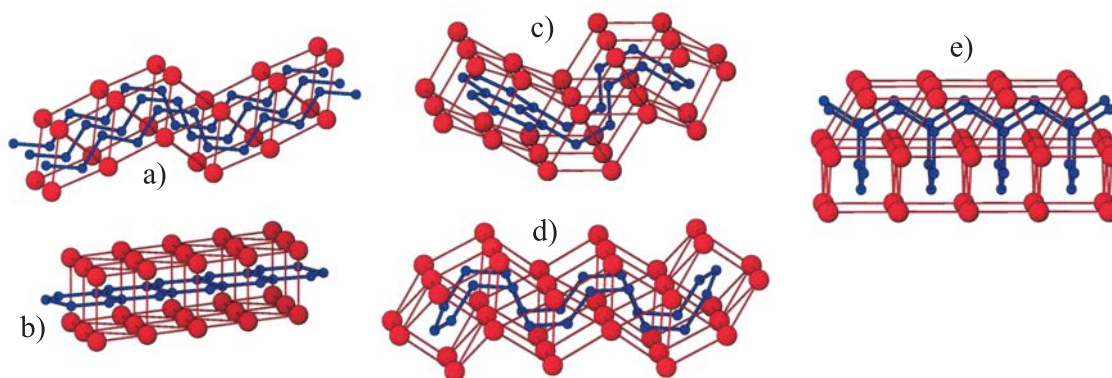


Figure 6: Building blocks in rare earth metal halide silicides. Si and RE are represented by blue and red spheres, respectively. The shown units are 2-dimensionally connected to slabs RE-(Si-Si)-RE. The halogen atoms are omitted.

- a): Si zig-zag-chains with the La environment in  $La_3Cl_2Si_3$ .
- b):  $Si_6$  rings with the RE environment in REISi (RE=La, Ce, Pr).
- c): Condensed  $Si_6$  and  $Si_{14}$  rings with the La environment in  $La_4I_3Si_4$ .
- d):  $Si_{22}$  rings with the La environment in  $La_5I_3Si_5$ .
- e):  $Si_{12}$  rings with the La environment in  $La_6Br_3Si_7$ .

In the structures of REISi and La<sub>3</sub>Cl<sub>2</sub>Si<sub>3</sub> all prisms are orientated in the (p) mode and they are connected via the square faces, all in cis-conformation for REISi to form flat sheets, and in trans, cis, trans, cis ··· -conformation with slightly corrugated slabs for La<sub>3</sub>Cl<sub>2</sub>Si<sub>3</sub>, respectively. The occupation of the centers of the prisms by silicon atoms leads to infinite Si zig-zag-chains (Fig. 6 a)) with Si<sup>2-</sup> ions for La<sub>3</sub>Cl<sub>2</sub>Si<sub>3</sub> and to planar Si<sub>6</sub> rings (Fig. 6 b)), which are two-dimensionally connected, for REISi, respectively.

In the structures of La<sub>6</sub>Br<sub>3</sub>Si<sub>7</sub>, La<sub>4</sub>I<sub>3</sub>Si<sub>4</sub> and La<sub>5</sub>I<sub>3</sub>Si<sub>5</sub> the trigonal RE prisms are fused in both (p) and (o) modes. For La<sub>4</sub>I<sub>3</sub>Si<sub>4</sub> (Fig. 6 c)) double-strings of La<sub>6</sub> prisms (o) are alternately condensed with prisms (p) to form corrugated layers. The parallel linked prisms correspond to a section of the β-ThSi<sub>2</sub> structure containing a ribbon of trans-condensed Si<sub>6</sub> rings. The occupation of the (o) prisms by Si atoms together with the connection of these atoms with Si<sub>6</sub> rings leads to the hitherto unknown Si<sub>14</sub> rings. In contrast to the nearly planar Si<sub>6</sub> rings (deviation from planarity less than 5°), the Si<sub>14</sub> rings are strongly bent (115°).

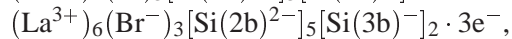
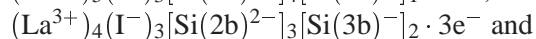
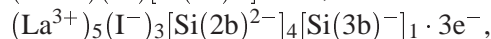
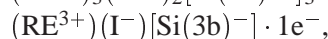
A similar arrangement of corrugated layers is found in La<sub>5</sub>I<sub>3</sub>Si<sub>5</sub> (Fig. 6 d)). A prism (o) is followed by eight prisms (p). Fusion through common rectangular faces for (o) prisms leads to chains, and for eight prisms in (p) orientation to ribbons. Chains and ribbons together form layers, containing Si<sub>22</sub> rings. Alternatively the structure of La<sub>5</sub>I<sub>3</sub>Si<sub>5</sub> can be described in terms of a combination of sections of the α- and β-ThSi<sub>2</sub> structural types. A block of α-type in which an (o) prism surrounded by (p) prisms on both sides is followed by a section of the β-type with (p) prisms in cis, trans arrangement. This formal decomposition of the structure indicates that besides La<sub>5</sub>I<sub>3</sub>Si<sub>5</sub> further compounds with a general composition (RE<sub>2</sub>Si<sub>2</sub>X)<sub>a</sub>(RE<sub>3</sub>Si<sub>3</sub>X<sub>2</sub>)<sub>b</sub> may exist, where the coefficients a and b denote the number of condensed blocks of the α- and

β-ThSi<sub>2</sub> structure type, respectively. The variation of a and b would allow different Si<sub>n</sub> ring sizes to be synthesized. In La<sub>5</sub>I<sub>3</sub>Si<sub>5</sub> (a = b = 1), the ring size corresponds to Si<sub>22</sub> and the rings are condensed into layers. For La<sub>3</sub>Cl<sub>2</sub>Si<sub>3</sub> with a = 0 and b = 1, Si zig-zag-chains are found.

In La<sub>6</sub>Br<sub>3</sub>Si<sub>7</sub> (Fig. 6 e)) double-strings of (p) and triple strings of (o) prisms are connected through rectangular faces, which are condensed into layers. The occupation of the centers of the (o) prisms leads to Si zig-zag-chains, which are closed by the Si atoms in the (p) prisms to Si<sub>12</sub> rings. The same Si<sub>12</sub> rings are observed in the structure of α-ThSi<sub>2</sub>, but three-dimensionally connected.

In all these structures the RE–(Si–Si)–RE slabs are connected via halogen atoms. In REISi flat sheets of the I atoms surround the slabs on both sides, in La<sub>4</sub>I<sub>3</sub>Si<sub>4</sub> part of the I atoms belong to only one slab, and others connect adjacent slabs, and in the other three structures slightly puckered monolayers of halogen atoms are arranged between neighboring sheets.

Within the Zintl-Klemm formalism with respect to the bonding b for Si the description of these compounds corresponds to:



respectively. One or three electrons per formula unit occupy bands with RE–RE bonding character. In agreement with the observed metallic conductivity and the results of band structure calculations, these electrons are delocalized. The number of electrons transferred from the REX<sub>n</sub> framework is strictly correlated with the size of the observed Si Zintl anion: 1.00e<sup>-</sup>/Si for REISi results in Si<sub>6</sub>, 1.50e<sup>-</sup>/Si for La<sub>4</sub>I<sub>3</sub>Si<sub>4</sub> in Si<sub>6</sub> and Si<sub>14</sub>, 1.71e<sup>-</sup>/Si for La<sub>6</sub>Br<sub>3</sub>Si<sub>7</sub> in Si<sub>12</sub>, 1.80e<sup>-</sup>/Si for La<sub>5</sub>I<sub>3</sub>Si<sub>5</sub> in Si<sub>22</sub> rings and 2.00e<sup>-</sup>/Si for La<sub>3</sub>Cl<sub>2</sub>Si<sub>3</sub> in Si zig-zag-chains, respectively.