

Ternary Rare Earth Metal Silicides $RE_2RE'_3Si_4$ with Orthorhombic Sm_5Ge_4 or Tetragonal Zr_5Si_4 Type Structure

Ute Ch. Rodewald^a, Birgit Heying^a, Dirk Johrendt^b, Rolf-Dieter Hoffmann^a, and Rainer Pöttgen^a

^a Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Straße 8, D-48149 Münster, Germany

^b Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstraße 5 – 13 (Haus D), D-81377 München, Germany

Reprint requests to R. Pöttgen. E-mail: pottgen@uni-muenster.de

Z. Naturforsch. **59b**, 174 – 181 (2004); received December 12, 2003

Dedicated to Professor Ingo-Peter Lorenz on the occasion of his 60th birthday

Ternary silicides $RE_2RE'_3Si_4$ ($RE = La, Ce$; $RE' = Y, Lu$) were synthesized by arc-melting of the elements. Single crystals were grown by annealing the arc-molten buttons slightly below the melting points in water-cooled silica tubes in an induction furnace. Five silicides $RE_2RE'_3Si_4$ were investigated by X-ray powder and single crystal diffraction: Zr_5Si_4 type, $P4_12_12$, $a = 779.4(3)$, $c = 1441.3(9)$ pm, $wR2 = 0.072$, 1806 F^2 values, 45 variables for $La_{1.72(4)}Y_{3.28(4)}Si_4$, $P4_32_12$, $a = 769.92(7)$, $c = 1412.3(1)$ pm, $wR2 = 0.079$, 1846 F^2 values, 45 variables, BASF = 0.36(4) for $La_{1.72(2)}Lu_{3.28(2)}Si_4$, $P4_12_12$, $a = 778.6(1)$, $c = 1433.9(3)$ pm, $wR2 = 0.054$, 1910 F^2 values, 46 variables, BASF = 0.34(4) for $Ce_{1.82(6)}Lu_{3.18(6)}Si_4$, $P4_32_12$, $a = 778.8(3)$, $c = 1436.0(10)$ pm, $wR2 = 0.166$, 1916 F^2 values, 45 variables for $Ce_{1.71(7)}Y_{3.29(7)}Si_4$, and Sm_5Ge_4 type, $Pnma$, $a = 749.2(2)$, $b = 1484.2(7)$, $c = 780.3(2)$ pm, $wR2 = 0.070$, 1956 F^2 values and 49 variables for $Ce_{1.47(3)}Y_{3.53(3)}Si_4$. The local coordinations of both structure types are very similar, *i. e.* CN 18, 16, and 14 coordination polyhedra for the $RE1$, $RE2$, and $RE3$ atoms. The main structural motif is the eightfold coordination of the $RE3$ positions by rare earth metal atoms. These slightly distorted $RE_2RE'_3$ cubes are condensed *via* common corners (Zr_5Si_4 type) or *via* common edges (Sm_5Ge_4 type). All silicon atoms in these silicides form Si_2 pairs at Si–Si distances ranging from 254 to 258 pm. DFT band structure calculations confirm the metallic character of both silicides and the trivalent state of cerium in Ce_5Si_4 . The COHP analysis (Crystal Orbital Hamilton Population) of the Si–Si bonds shows a significant occupation of Si–Si antibonding orbitals, which is partially compensated by a Si–Si π^* , $\sigma^* \rightarrow Y-4d$ (Ce-5d) back donation.

Key words: Silicide, Crystal Structure, Solid State Synthesis, Chemical Bonding