High-Pressure Synthesis of Intermetallic Framework Compounds $RESi_3$

Teuta Neziraj[1], Steffen Wirth[1], Ulrich Schwarz[1], Yuri Grin[1]

[1]Max-Planck Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, teuta.neziraj@cpfs.mpg.de

Covalent framework compounds are a very interesting class of materials regarding their structural diversity and their physical properties. Earlier investigations of the reactions between silicon or germanium with rare-earth metals (RE) have led to the discovery of a rich variety of binary phases and new structural patterns by applying high-pressure synthesis [1,2]. According to the phase diagrams of rare-earth elements with silicon, synthesis at ambient pressure yields $RESi_{2-x}$ as the silicon-richest phase. In an effort to realize an increased number of Si-Si contacts at ambient conditions, silicon-rich phases need to be synthesized at high-pressure and then quenched. The high-pressure phases usually exhibit multicenter interactions and enhanced coordination numbers [3]. Following this principle, a series of five $RESi_3$ (RE= Gd, Tb, Dy, Er, Tm) compounds was synthesized and characterized, thus expanding the map of binary silicides.

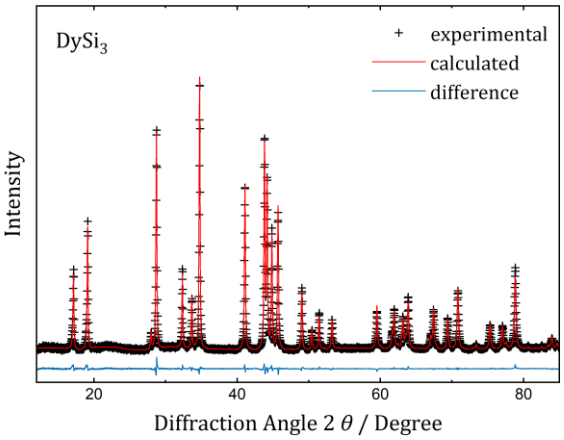

Fig. 1 Synchrotron powder XRD pattern of $DySi_3$ and results of Rietveld refinement.

The metastable binary rare-earth trisilicides $RESi_3$ were obtained by high-pressure high-temperature synthesis (9.5 GPa, 823-923 K). At ambient pressure, the compounds decompose exothermally upon heating into Si and $RESi_{2-x}$. Powder diffraction data refinements (Fig. 1) reveal that the crystal structure of the compounds is isotypic to that of $CaGe_3$ [4]. The values of cell parameters, respectively the cell volume, decrease from Gd to Tm as it is expected due to the lanthanide contraction.

Magnetic measurements on compounds $RESi_3$ reveal for $DySi_3$ (Fig. 2) Curie-Weiss paramagnetic behaviour with a calculated effective moment $\mu_{eff} = 10.63\ \mu_B$ which is consistent with the $^6H_{15/2}$ ground state of the $4f^9$ configuration of dysprosium (Dy^{3+}, $\mu_{eff} = 10.65\ \mu_B$). The value of Θ = -4,2 K determined from the linear fit, indicates antiferromagnetic ordering of $DySi_3$.

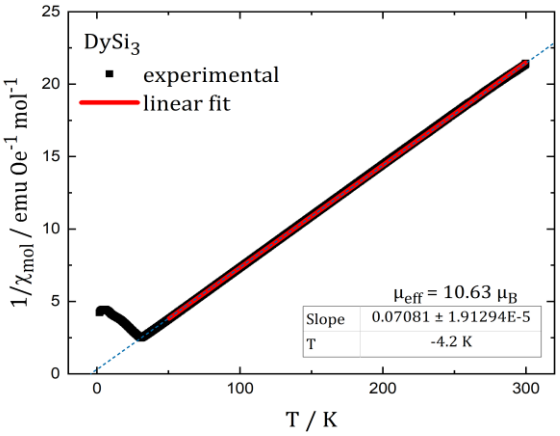

Fig. 2 Inverse corrected magnetic susceptibility $1/\chi$ of $DySi_3$ against temperature T.

[1] Schwarz, U.; Wosylus, A.; Rosner, H.; Schnelle, W.; Ormeci, A.; Meier, K.; Baranov, A.; Nicklas, M.; Leipe, S.; Müller, C. J.; Grin, Yu. Dumbbells of five-connected silicon atoms and superconductivity in the binary silicides MSi_3 (M = Ca, Y, Lu). J. Am. Chem. Soc. 2012, 134, 13558−13561.

[2] Nishikawa, T.; Fukuoka, H.; Inumaru, K. High pressure synthesis and electronic structure of a new superconducting strontium germanide ($SrGe_3$) containing Ge_2 dumbbells. Inorg. Chem. 2015, 54, 7433−7437.

[3] Wosylus, A; Meier, K.; Prots, Y.; Schnelle, W.; Rosner, H.; Schwarz, U.; Grin, Yu. Unusual Silicon Connectivities in the Binary Compounds $GdSi_5$, $CeSi_5$, and Ce_2Si_7. Angew. Chem. Int. Ed. 2010, 49, 9002-9006.

[4] Schnelle, W.; Ormeci A.; Wosylus A.; Meier K.; Grin J.; Schwarz U. Dumbbells of Five-Connected Ge Atoms and Superconductivity in $CaGe_3$. Inorg. Chem. 2012, 51, 10, 5509−5511.