Abstract

The scope of the present thesis is the synthesis and analysis of structural and physical properties of filled Pt-Ge-based skutterudites, $EpPt_4Ge_{12-x}Sb_x$ (Ep =electropositive elements) and $LaPt_{4-x}M_xGe_{12}$ (M = transition metal elements), with specifically chosen substituents. Skutterudites like {Ep=La,Ba,Sr}Pt₄Ge₁₂ are ternary cage forming compounds, crystallizing in a bcc-type structure, and p-type materials. They exhibit a superconducting ground state, with T_c around 8 K (La) or 5 K (Ba, Sr), concomitant with rather poor thermoelectric capabilities. Furthermore, LaPt₄Ge₁₂ is occasionally discussed to be a two-gap superconductor. Based on partial substitutions of Ge by Sb, previous results revealed a suppressed superconducting state and a simultaneous shift towards enhanced thermoelectric properties in LaPt₄Ge₁₂. Previous DFT calculations already revealed that in $LaPt_4Ge_{12-x}Sb_x$, for x=5, a gap opens and x>5 should be a n-type material. Thus, $\{La, Ba, Sr\}Pt_4Ge_{12-x}Sb_x$ sample series were synthesized by arc melting, analyzed by EPMA and XPD, and several temperature as well as field dependent physical properties were studied. For $LaPt_4Ge_{12-x}Sb_x$, a sample series with three compounds at the solubility limit was fabricated. Here, a maximum solubility of x = 4.85 and a thermoelectric figure of merit around 0.16, at 750 K, could be achieved. Moreover, $\{Ba,Sr\}Pt_4Ge_{12-x}Sb_x$ sample series, with nine different antimony contents each, from x=0 up to the solubility limit were produced. Experimental results suggest BCS type-II superconductivity for both sample series up to x = 2.71 (Ba) and x = 2.56 (Sr). Moreover, the results indicate a vanishing superconducting state in both cases for x > 4. DFT calculations locate the Fermi energy close to (or into) a pseudogap for x=6 and indicate therefore n-type behavior for x > 6. Here, a maximum solubility x = 6.06 (Ba) and x = 5.73 (Sr) could be achieved. However, both exhibit still p-type conductivity, in case of x = 6.06(Ba) caused by a slightly reduced amount of filler atoms. Nevertheless, a four-fold (Ba) and six-fold (Sr) larger power factor in comparison to x=0, at roughly 800 K, can be stated at the solubility limit. Apart from that, compounds with partial substitutions of Pt by Au in {La,Ba}Pt₄Ge₁₂ were recently published. Based on this, small samples of $LaPt_{4-x}M_xGe_{12}$, where M = Ni, Pd, Fe, Co, Rh, Ir, Cu or Agand x = 1 were produced. A subsequent analysis by EPMA indicated a maximum solubility for Ni. Thus, a sample series of $LaPt_{4-x}Ni_xGe_{12}$, with x=0, x=0.09and x = 0.18, was synthesized and physical properties were measured. Taking an identified La₂Pt₃Ge₅ superconducting secondary phase into account $(T_c \approx 8)$ K), the compounds can be also assumed to be BCS type-II superconductors with $T_c \approx 7.8 \text{ K (for both } x = 0 \text{ and } x = 0.09) \text{ and } T_c \approx 7 \text{ K (} x = 0.18). \text{ However,}$ unconventional superconductivity can not be fully excluded.