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Preparation of doped Pr skutterudites

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Various anomalous physical properties of Pr skutterudites PrT_4X_{12} (T=Fe, Ru, Os and X=P, As, Sb, Bi) are attracted much attention of many researchers. Replacing T- or X-element by another T- or X-element, Pr skutterudites drastically change their characteristic physical properties such as metal-insulator transition, unusual heavy-fermion state, unconventional superconducting state and so on. In these compounds, hybridizations among d-, p- and f-orbits are thought to play an important role, and they can be tuned by pressure or partial substitution of T- or X-element. Here, it should be noted that variation of the physical properties under the physical pressure is probably different from that caused by the chemical pressure of the partial substitution. Therefore, the comparison of both pressure effects is expected to lead to understanding the physical properties of Pr skutterudites well. Furthermore, new phenomena are also expected, because doped Pr skutterudites are thought to be new materials. So, we attempted to grow single crystals of Pr skutterudites partially substituted by another T- or X-element at a first stage of our research plan.

1. $PrT_4(Sb_{1-x}As_x)_{12}$ and $PrT_4(Sb_{1-x}Bi_x)_{12}$

Among PrT_4X_{12} series, PrT_4As_{12} and PrT_4Bi_{12} are missing, and this missing prevents the systematic study of PrT_4X_{12} series. Preparation of these compounds is probably very difficult. Therefore, we tried at first to grow As- or Bi-doped $PrRu_4Sb_{12}$ from Sb-rich solution using the self-flux method. In the case of As-doping, although we added As about 10 % to starting materials, only 1 % of Sb was replaced by As. Furthermore, any trace of Pr skutterudite was not observed in X-ray diffraction measurement when a larger amount of As was added. On the other hand, in the case of the trial for Bi-doping, any trace of Bi was not detected in the obtained crystals. The Bi-doping is thought to be more difficult than the As-doping probably due to a larger ionic radius of the Bi ion.

2. $Pr(Os_{1-x}Ru_x)_4X_{12}$

As is well known, $PrRu_4Sb_{12}$ is thought to be a conventional superconductor with T_c=1.0 K, while $PrOs_4Sb_{12}$ is the first Pr-based heavy fermion superconductor. Furthermore $PrRu_4Sb_{12}$ shows multiple superconducting transitions. Therefore, new phenomena are also expected even by the partial replacement of T element. Recently, N. A. Frederick *et.al.* succeeded to grow single crystals of $Pr(Os_{1-x}Ru_x)_4Sb_{12}$. From the Ru-concentration dependence of T_c, they predicted that the two types of superconductivity compete at x=0.6. [1] We also tried to prepare Ru-substituted $PrOs_4Sb_{12}$ and succeeded to grow single crystals of $Pr(Os_{1-x}Ru_x)_4Sb_{12}$ with x =0.4 and 0.75, of which T_c is less than that of non-doped $PrOs_4Sb_{12}$.

Furthermore, we tried to prepare $Pr(Os_{1-x}Ru_x)_4P_{12}$ using the Sn-flux method and obtained their small single crystals at present stage.

[1] N. A. Frederick, T. D. Do, P. -C. Ho, N. P. Buch, V. S. Zapf and M. B. Maple, Phys. Rev. B **69**, 024523 (2004).