

High-pressure synthesis and properties of filled skutterudite compounds with group 14 elements in the host network and related comopunds

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The filled skutterudite structure is composed of corner sharing MX_6 octahedra and guest atoms, where M and X represent transition metals and pnictogens. When the present study started, only pnictogen atoms can form the host network of filled skutterudite compounds. Therefore, I attempted to prepare a new type compound containing heteroatoms in the host cage, and found that germanium can participate in the host network[1]. The compounds obtained are listed in Table 1. All compounds in Table 1 were prepared by using high-pressure and high-temperature reactions. The susceptibilities of $LnM_4Sb_9Ge_3$ except for La compounds obey the Curie-Weiss law and the oxidation states of rare earth ions are 3+. They do not exhibit superconductivity to a temperature of 2 K. However, new superconductors were recently discovered by Bauer et al.[2,3] Those became the first compounds of which icosahedral cages are formed only by Ge atoms.

Table 1 includes new skutterudite compounds with alkaline earth metals as well as compounds having anions at the guest ion sites. $I_{1-x}M_4Sb_{12}$ M = Rh and Co are the first examples of anion-filled skutterudite compounds. They can be obtained only if the constituents are reacted under high-pressure and high-temperature conditions.

I have also studied compounds having rare earth ions situated in highly-symmetric sites. $CeGe_3$ has the famous Cu_3Au structure and exhibits a metallic property.

The magnetic susceptibility, thermoelectric power, and heat capacities for some of these compounds are discussed.

Table 1 New compounds obtained in the high-pressure reactions

Systems	compounds
$LnRh_4Sb_9Ge_3$	$Ln = La, Ce, Pr, Nd, \text{ and } Eu$
$LnCo_4Sb_9Ge_3$	$Ln = La, Ce, Pr, Nd$
$LnCo_4P_9Ge_3$	$Ln = La$
$I_{1-x}M_4Sb_{12}$	$M = Rh \text{ and } Co$
$BaIr_4P_{12}$	
$LnGe_3$ with the Cu_3Au type structure	$Ln = Ce \text{ and } Sm$
$LnGe_5$ with $LaGe_5$ type structure	$Ln = Ce, Pr, \text{ and } Nd$

[1] H. Fukuoka and S. Yamanaka, *J.AlloysCompd.* **461** (2008) 547-550.

[2] E. Bauer, A. Grytsiv, X-Q. Chen, N. Melnychenko-Koblyuk, G. Hilscher, H. Kaldarar, H. Michor, E. Royanian, G. Giester, M. Rotter, R. Podloucky, and P. Rogl, *Phys.Rev.Let.* **99** (2007) 217001.

[3] D. Kaczorowski, and V. H. Tran, *Phys.Rev.* **B77** (2008) 180504.